

Read Synthetic Rock

# CHEMISTRY

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Editorial:  
The Phase Rule  
Inside Front Cover

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# The Phase Rule

► THE SWIFT TRANSITION from abstract theory, investigated for its own interest, to intensely practical application is nowhere better shown than in the history of the Phase Rule. Founded in the 1870's by J. Willard Gibbs, on mathematical theory too deep for most of his hearers, its development and application to chemical problems was carried on in Europe, especially by Roozeboom and other Dutch chemists, before the turn of the century. It was then all theory. Who cared about so insignificant a quantity as the vapor pressure of ice?

But as patient laboratory men took down the thousands of readings of thermometers and manometers, which were necessary to determine the characteristic curves that illustrate the "Classic" on pages 28-40 in this month's CHEMISTRY, new understanding began to dawn as to why materials are as we see them.

So commonplace a question as why table salt is so absurdly wet in summer, so practical a problem as how to keep the water in automobile radiators from freezing, so important a factor as how to make alloys at less cost are all answered by the Phase Rule, in satisfyingly general terms.

Still another application of the Phase Rule is now coming into prominence. This is well illustrated by the leading article in the current issue of this magazine. Scientists are investigating the series of compounds possible (and impossible) between the elements which make up the earth's crust. By this means only can we short-circuit the theories and controversies that marked the early days of geology, and really learn something about how the structure of the earth came to be. Add our new-found knowledge of transmutation, and we should have the key to provision of essential materials anywhere.

This is not to imagine that every possible chemical transformation would be worth while. Building a new continent out of the calcium in sea water, or colonizing the antarctic with uranium for fuel are among the wilder speculations. Chemical evolution will probably follow a more practical course, but perhaps it will reach a better goal, as unforeseen by us as our own civilization was to the savage who froze to death on the outcrop of a seam of coal.

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► MODELS of the crystals they are able to make are exhibited by Dr. N. L. Bowen and Dr. O. F. Tuttle of the Geophysical Laboratory, Carnegie Institution, at Washington, D. C. Heat and pressure applied to the pure chemicals result in crystals like those found in nature.

## Synthetic Rock

by HELEN M. DAVIS

► ADD to the achievements of the modern scientist a new accomplishment. He has succeeded in making a rock. He has known for nearly two hundred years exactly what rocks are made of, and he has argued for about as long over theories of how they occur. But only now has he reached enough understanding of nature's

processes to be able to duplicate one of the materials nature strews around in such abundance.

In a report just issued, the Geophysical Laboratory of the Carnegie Institution of Washington announces that scientists of its staff have found it possible to make, in special apparatus they have devised, all the more

common natural anhydrous silicates of magnesium, and a couple of the hydrous ones, of which the best known is talc.

Talc, which is the original material from which talcum powder is made, has a fairly simple chemical formula. The same substance was formed in the apparatus at the Geophysical Laboratory when magnesium silicate in the form of synthetic serpentine was heated to 700 degrees, centigrade, (about 1300 degrees, Fahrenheit) under pressure of 30,000 lb. per sq. inch. The scientists are trying to learn whether they can make well-known minerals under conditions likely to occur within the earth.

"Hard as a rock" is a proverbial expression, but, considering the thousands of years that man has been using rocks for weapons, tools and building materials, it is remarkable how little he really knows about them.

Geologists separate rocks from minerals, a term which they reserve for ores of metals, or other specific materials valuable enough to dig for, deep into the earth. Rock is the hard stuff down below the soil that they have to break and dig through, or blast away, to reach the gold or the iron or the coal they want to mine.

Rocks are the bones of Mother Earth, according to the ancient Greeks. In their version of the story of the Flood, Deucalion and Pyrrha, counterparts of "Mr. and Mrs. Noah," were commanded by a divine voice to throw over their shoulders "the bones of their mother." These sole survivors of the human race solved the heavenly riddle by throwing rocks behind them. The rocks were transformed into young men and women,

and the repopulation of the earth was thus assured.

The rocks that Deucalion and Pyrrha must have found lying on the surface of the earth were weathered fragments broken off the great mass of rock formations that do, indeed, form the solid framework of our earth. How this material comes to be formed has puzzled the scientifically-minded since long before the time of the Greeks, but there was very little they could do about trying to duplicate nature's rock-making methods until our own day.

First it was necessary to know what kinds of rocks there are and something about their occurrence. This was being worked out by early geologists about 200 years ago. Their theories were crude, and they were much confused by their notion that everything they observed had to be fitted into a chronology determined by the Biblical accounts of Creation and the Flood. Limited by their short time scale, the vast geological changes they recognized in the earth had to be accounted for by cataclysmic forces shifting mountain masses around with a violence which, they hoped, had permanently abated before the present time. Very slowly the early geologists learned that quieter forces can accomplish great results if only a longer time is allowed for their action.

Volcanoes naturally made a great impression on early geologists, who were inclined to consider them the cause of all primary rock-building. In a later reaction against the catastrophic theory of geology, scientists newly conscious of chemistry tried to explain rock formation in terms of precipitation from solution in water.

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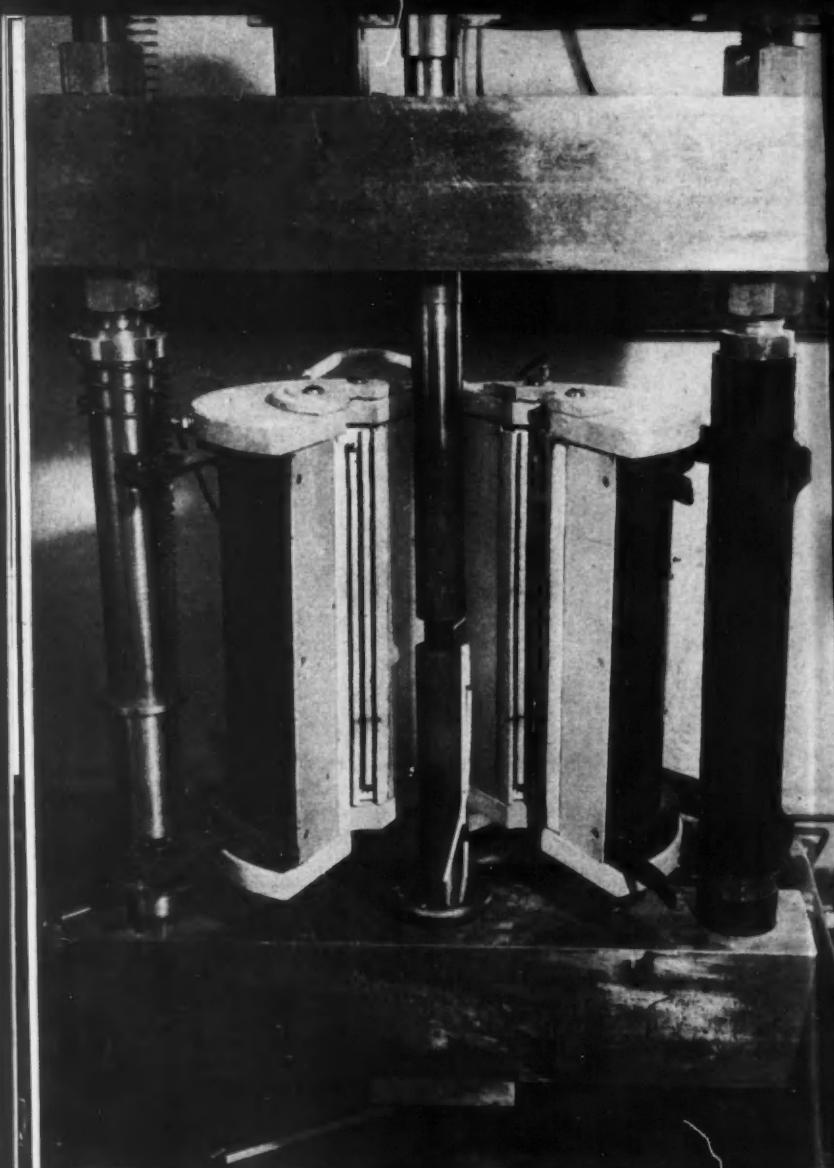
► TINY CAPSULES hold the chemicals which are treated to form synthetic minerals. A straightened-out paper clip points to two of the capsules laid out on a sheet of diagram paper.

The controversy between the "vulcanists" and the "neptunists," as they called each other, went on until wider observation led to better understanding. Later geologists learned how granites are eroded away by weathering and remade into sedimentary deposits, and how limestone is laid down in shallow seas and built around the shells of marine animals.

But understanding the forces that rework rocks on the surface of the earth is different from understanding

how those rock masses originate. The geologist still refers to such primary rocks as "igneous" and believes their formation is due to heat and pressure greater than any we ordinarily experience, although he does not necessarily believe they have been melted in the fires of a volcano.

After learning how rocks are formed, it was necessary to find what they are made of, and chemists long ago determined that many of them are silicates. But silicates are materials



► THE FURNACE where minerals are made is opened to show the capsule in the pressure apparatus and the heating coils which surround it.



► MINERALS and gases from this active volcano, Santiaguito, in Guatemala, are also being analyzed in the Carnegie Institution's rock study program. Scientists believe it is possible that rocks hot from the crater have a different structure from those from the same source after they have cooled, and the gases have escaped.

which have been singularly unsatisfactory for chemists to work with until very recently. New interest in these compounds is one of the reasons the Geophysical Laboratory is again taking up its program of rock study, part of which was begun before the interruption of the war.

With newly designed high-pressure apparatus into which chemicals and water can be introduced under pressure and the whole system heated to a high temperature, the Carnegie scientists are studying series of compounds formed by reactions between

magnesium oxide ( $MgO$ ), silica ( $SiO_2$ ) and water ( $H_2O$ ). These give the characteristics of the simple magnesium silicates, which have already been made.

"The magnesium silicates formed in the experiments now completed," states the Carnegie Institution report, "are common in certain varieties of igneous and metamorphic rocks, and a knowledge of their ranges of stability with respect to pressure and temperature would throw light on the conditions of their formation in nature."

Working according to rules of chemical equilibrium formulated within the past century by the late Josiah Willard Gibbs\* of Yale University, chemists are now able to map out all the possible compounds of a system such as the  $MgO - SiO_2 - H_2O$  one on which the Carnegie Institution scientists began to work. By varying the amounts of the different materials systematically and studying the effect of heat and pressure on different batches, charts of all the possible compounds in this system can be prepared, and known minerals of the same composition can be matched with these charts to learn the conditions under which these substances could, and could not, have been formed. With this knowledge, the scientist can, for the first time, feel that he has definite information about conditions deep down in the earth's crust where rocks composed of these minerals have been formed.

Many other series of experiments are planned by the Geophysical Laboratory. Those where water is introduced into the system they speak of as "wet silicate" problems. Those in which magnesia and silica are combined with another metallic oxide, for example that of potassium, without water, they call "dry silicate" problems. Some of these studies will throw light on the origin of granite. Others will give more knowledge about the chemical constitution of cement.

Several of the studies under way work with four components instead of three. In some of them the systems described above are studied with addition of iron compounds and lime. In another, a system of phosphates, such as make up rocks valuable for fertilizer, is being mapped. Problems connected with the occurrence of gold and silver in silicate rock, and of replacement of silicon by boron and germanium are also being undertaken. And in another part of the work of the Geophysical Laboratory, studies of material from the active volcano, Santiaguito, in Guatemala, is being collected to study the large amounts of hydrochloric and sulfuric acids escaping from the crater. Escape of these volatile materials, the scientists believe, has caused important changes in the minerals composing the "fresh" rock coming from this volcano during the time it has been pushed up from the fiery depths.

The manufacture of synthetic rock in the laboratory thus promises to solve some of the mystery of how the earth was put together. But, like so many other investigations for science' sake, we may be hearing, one of these days, about new kinds of synthetic rock that are useful for special practical purposes. There may be born of the high temperatures and high pressures used more stable building cements, or more concentrated fertilizers to grow the food of the future.

\* See *Classic of Chemistry*, page 28.

### *On the Back Cover*

► SWALLOW-TAILED twin crystals seen through the microscope show that orthoclase, found in nature in the clay used for china glaze, has been formed in the laboratory.

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## Atomic Energy Commission Makes Supply Available

# Stable Isotopes for Research

► MORE THAN 100 hard-to-get varieties of 29 different elements are now available from the Atomic Energy Commission for scientific research as a peaceful by-product of work on the mass production of uranium 235 for the atomic bomb at Oak Ridge, Tenn.

The new research materials are stable isotopes, atoms of elements which have the chemical properties of the element but different weights. Stable isotopes do not give off radiation as do the radioactive isotopes.

Unlike the radioactive varieties, the stable isotopes now available are not direct by-products of the fission elements, the Commission emphasized. The new supply of stable isotopes is possible because of research and development in the production of the atomic bomb elements, while the radioactive forms are produced in the chain-reacting pile. The Commission has been producing radioactive isotopes at Oak Ridge and selling them for research purposes since August, 1946.

Chief benefits predicted from the new supply of stable isotopes are for tracer work and other studies under conditions where radioactive isotopes cannot be used, for the production of certain radioactive isotopes and for spectroscopic studies of individual isotopes.

Radioactive isotopes have a harmful effect on human tissue which makes them dangerous for some types of re-

search and the radioactivity of some of them is limited to a few hours. Stable forms now available can be used in these cases. New radioactive isotopes may be possible starting from the stable form, the Commission suggested. Studies of the atomic structure of the new isotopes and bombardments with various particles may result in new atomic developments.

Most of the stable isotopes made available by the Commission are produced at the electromagnetic plant at Oak Ridge operated by Carbide and Carbon Chemicals Corporation, where the first mass production of uranium isotope 235 was achieved. By altering the equipment, it is now possible to separate isotopes of other elements.

Stable isotopes of elements which are normally gases or elements which are heavier than lead and a few other isotopes are not being concentrated electromagnetically in this program.

The new stable isotopes will not be sold, as the radioactive elements are, but they will be loaned to researchers for \$50 per sample upon approval of allocations. Limited supply and high cost of production make the loan stipulation necessary, the Commission explained.

Highest priority will be given for research which will not use up or adulterate the material, and a statement will be required to account for material not returned or returned in adulterated form.

How To Find It  
How To Get It Out

## Finding New Oil Fuel Resources

by A. C. MONAHAN

► THERE IS PLENTY of oil in the earth's crust, scientists say. The problem is how to find it, and then how to get it out. The greatest untapped source is the 10,000,000 square miles of continental shelf that extends from a few to a few hundred of miles underwater from the shores of continents and islands.

There is also plenty of unfound oil in dryland areas, they believe. But it is deep down, perhaps a mile or more, below the present known deposits. Or it is beyond the Arctic Circle, buried below accumulated ice and hundreds of feet of frozen earth. And perhaps it is in accessible places but not in the ordinary petroleum traps from which most crude oil is now obtained. To locate this oil, new scientific instruments are needed. Geophysicists are working frantically to develop them.

The petroleum geologist is the number one man in oil exploration. There is no divining rod that will locate petroleum. The first step, after surface surveys, is a wide and intensive study of the underlying strata of the earth in the general type of geological structure favorable to oil formation. In these every bit of geological information must be taken under consideration. Included are rock outcrops on the surface, crust structures within mines if any are in the region, and the logs of every deep well drilled in the general area

whether for deep water, minerals or any other purpose.

Geologists now know the crust of the earth from the Arctic to the Antarctic well enough to be able to plot roughly the areas favorable for finding petroleum deposits. They call such regions "petroliferous." These areas now must be closely studied by geologists and geophysicists, the latter using such instruments as the seismograph, gravity meter and the magnetometer.

One noted petroleum geologist estimates that there are 1,000,000,000,000 barrels of oil in the world's continental shelf. He is Wallace E. Pratt, former vice-president of the Standard Oil Company of New Jersey, who has devoted much of his life to the application of geology to the discovery of petroleum. Exploration for this oil has not yet reached the drilling stage, except relatively near shore, but ocean-bred instrument studies are being made in the Bahama seas, some 200 miles off the coast of southern Florida. The scientists are working deep in the water under diving bells.

There are, of course, many producing oil wells in the ocean off-shore from California, Texas, Louisiana, Venezuela and elsewhere. They are largely in proven areas that extend under the sea from producing fields ashore. Three wells have been drilled from 10 to 30 miles out from Louisiana in the Gulf of Mexico, and several others are planned.

Much of the petroleum in conti-

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ntional shelves can never be recovered because of the depth of the water over them and their location, such as in the Arctic ocean. No one has yet figured out the best way to mine the underocean oil. At the 10-mile well off Louisiana, the plan used was relatively simple because the water at the site is only 16 feet deep at low tide.

A platform on piles was erected 20 feet above mean high water. This gives protection against high waves. The platform is large enough to hold all drilling equipment, fuel, fresh water and standby units.

One suggestion of how to tap the continental shelf oil is by the use of anchored diving bells, large enough to house a derrick and drilling rig. Underwater pipelines would bring the oil ashore. Another is to use large floating platforms of the type once proposed for mid-ocean landing fields for transatlantic airplanes.

A third suggestion is to tunnel out from the shore through the ocean bed to the oil sands and drill the wells in the tunnel.

It is not expected that there will be any attempts to tap oil supplies deep under the ocean while a plentiful supply can be obtained otherwise. There is much petrolierous area in the world as yet unexplored. Active explorations by instruments and core-drilling are underway in many of them, including Australia, a continent producing no petroleum as yet, Siberia, Alaska and in both the Americas.

There is also the possibility that continental shelf oil may never be needed, particularly if liquid fuels can be obtained cheap enough from

coal, oil shale or natural gas. Liquid fuels from vegetation, such as alcohol, may also limit the need for gasoline.

Of more immediate importance than the oil in the continental shelf, of which the United States has a million square miles, is the hidden petroleum in petrolierous areas within the continent. About one-eighth of the petrolierous areas of the world are in America.

They are largely in the interior. One great area extends northwesterly from Texas, passing just east of Denver, through the Wyoming and Montana oil fields up to Calgary, Canada. After a break, it goes almost up to adjoin the North Alaska field now being drilled by the Department of the Navy.

Another area extends westward from the present Ohio and West Virginia fields to the Mississippi, covering Lower Michigan. Less promising geological formations exist in Florida, Southwest Alaska, Hudson Bay country and along the Arctic coast of North America. The Uinta Basin, eastern Utah, now under exploration, is expected to yield much oil.

To the layman any method of determining the deep underground structure of the earth without digging deep shafts or drilling wells seems a mystery. However, scientists are using several. The seismic, gravity and magnetic methods have proved most useful. Now technicians are attempting to employ induction currents and radio.

The seismic method, perhaps the most helpful of those used, employs the seismograph, best known to the public as the device used to detect

and record earthquake tremors. In this method, explosives are used near the surface to set up sound waves, some of which go downward deep into the earth. They are reflected back when they hit a dense layer of minerals. The reflections are recorded at several scattered stations; then the location of the layer is determined by mathematics.

In the gravity method, deviations in the direction of the force of gravity caused by dense underlying formations are measured. The magnetic method depends upon the influences of underground structures on a free-swinging magnetic needle. The instrument used is called a magnetometer.

Essentially a magnetic survey is a method of determining the contours of underlying granites and other formations known to scientists as the "crystalline basement." A knowledge of this basement, particularly in areas covered by marine sediments is of fundamental importance to oil exploratory work. The magnetometer, for detailed work, is ground-based, often trailer-mounted. For general preliminary surveys the same magnetometer which was trailed behind and under airplanes to detect submerged Nazi U-boats is employed. It has been used for greater details than can be obtained with planes, borne by a helicopter.

Several electrical methods have been tried to locate oil deposits. Now the use of radio seems promising. A government patent, No. 2,426,918,

issued Sept. 3, 1947, has recently been awarded to William M. Barret, Shreveport, La., for a method developed by him. He states that he has found earth layers do not quench electromagnetic waves of radio frequency as rapidly as had been assumed, so that he can project them into the ground and receive their echoes.

Another electrical instrument is under development in the New York laboratory of Frank Rieber, an inventor well known for his widely used refraction and reflection seismograph. The instrument will use radio reflections rather than shock waves by man-made explosions as with the seismograph.

Present exploratory instruments are successful in locating oil in what are known as traps formed in the earth's crust by overlaps and folding of underground strata. But all oil is not in such traps, Mr. Rieber believes. There is oil in traps of a different sort, widely spread in porous layers between other layers. He calls the first a structural trap; the second, a stratigraphic trap. The instrument on which he is working is primarily to discover the oil in these stratigraphic traps by locating porous layers and tracing them to spots where the oil might accumulate.

Present known oil reserves in the United States may become exhausted in from 15 to 30 years, as many believe, but oil men all seem to feel that undiscovered deposits will keep the country supplied for a much longer period than that.

## Salt Water With Crude Oil

► OIL-FIELD DISPOSAL of salt water raised along with the petroleum from deep underground is a troublesome and costly problem. How it was solved in the East Texas oil fields was told recently by W. S. Morris of the East Texas Salt Water Disposal Company.

The East Texas field, 42 miles long and from four to eight miles wide, is what geologists call a water-drive reservoir. Soon after the field was discovered in 1930, it was evident that large volumes of salt water would be produced in the course of the production of the oil. Early in 1936, the feasibility of returning the salt water to the sands from which it came was demonstrated. It is the salt-water disposal method now followed.

However, the cost of providing salt-water treating plants and injection wells was so great that only the larger oil companies could afford to make use of the method. The result was the organization early in 1942 of the company represented by Mr. Morris, which now has 38 injection wells and injects some 390,000 barrels of salt water a day. There are a total of 75 injection wells in the field. The other 37 wells return to the sands about two-thirds

as much water daily as the 38 operated by the East Texas Salt Water Disposal Company.

The salt water, after separation from the oil, is piped to concrete tanks. Ordinary treatment consists of aerating and the addition of chlorine, lime and alum, after which it is permitted to settle for 24 hours. In cases where open tanks are used in the collection, it is also necessary to control the growth of algae, fungi, and bacteria. The bacteria found in East Texas salt water are of the anaerobic sulfate-reducing type, identified as *Vibrio thermodesulfuricans*. Unless the water is thoroughly stabilized and all foreign matter removed, the sand face in the disposal wells becomes plugged, and the input sharply reduced.

In addition to the benefits of the increased recovery of oil and the elimination of pollution of the streams, the return of salt water to the reservoir has maintained the bottom-hole pressure to the extent that the use of artificial lift has been greatly reduced. It is estimated that as a direct result of the salt-water disposal program more than 600,000,000 barrels of additional oil will be recovered from the field.

## Automobiles and Oil Cracking

► PETROLEUM CRACKING to get more gasoline is now a 35-year-old process. The man who discovered how to do it was honored by the American Petroleum Institute, at its Chicago meeting, with its gold medal for distinguished service. The recipient was Dr.

William M. Burton, of Cambridge, Mass.

Dr. Burton became the first chemist employed by the Standard Oil Company of Indiana in 1890. Later he rose to the presidency, and held that position from 1918 until his retirement in

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1927. His invention was the Burton still, patented in 1913, at which time 12 were in operation.

Burton's still is one of the factors that made the twentieth-century automobile age possible. The rapid growth of the motor vehicle industry depended upon a plentiful supply of fuel. Without a cracking process, enough gasoline could not be produced to meet the demands, because only about 18% of the molecules in crude petroleum in its natural state is suitable to be included in gasoline.

When Dr. Burton began his serious work to find a suitable method for cracking crude he knew that some laboratory experiments indicated that the heavy or larger molecules in the petroleum could be broken by heat into smaller molecules. His discovery was the effectiveness of a combination of heat and pressure. At a pressure of 95 pounds per square inch and a temperature of about 750 degrees Fahrenheit, he found that part of the heavy crude would break down into gasoline and other petroleum products.

Catalytic cracking is a later development, and the Burton still now is obsolete. So, largely, are other thermal cracking processes following the Burton developments.

Catalytic cracking is based on the so-called Houdry process, developed in France but much improved in America. In this the catalyst used becomes clogged with carbon that later has to be burned out. In one American process, the catalyst, in the form of beads, passes through the reaction chamber in one direction while the vapors from the charging stock pass in the other. Before being repassed

through the chamber, the beads are burned clear of the carbon.

A catalyst is a substance introduced into the chamber where chemical reactions are taking place which does not itself enter chemically into the reactions but which in some mysterious way assists them. Its principal effect is, perhaps, to speed the reactions.

In the petroleum industry, in catalytic cracking the net effect is to change relatively high-boiling hydrocarbons to lighter products, such as gasoline and high-grade aviation fuels.

The selectivity of the catalyst is not a single property, Rodney V. Shankland and George E. Schmitkons of the Standard Oil Company (Indiana) told the American Petroleum Institute, but a category of properties measured by the influence of the catalyst on the product distribution. This is generally thought of in terms of the relative amounts and qualities of four products of cracking. These are coke, gas oil, gasoline, and gas. Coke and gas are usually considered undesirable products; hence rating catalysts in terms of coke and gas-producing tendency is important.

Messrs. Shankland and Schmitkons described a laboratory test method suitable for testing granular, powdered, or pilled catalysts for cracking activity and selectivity. Hubert McReynolds, of the Texas Company, described a quick method for determining the activity of cracking catalysts in powdered form. Other scientists described other methods.

The various test methods used fall into two principal groups, one based on a standardized laboratory cracking operation, the other on surface-area reactions.

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## German Gasoline Substitute Tried Here With Improvements

# Gas and Oil From Coal

► MOTOR FUEL SCARCITY in Germany during the war resulted in the development of coal gas enriched with methane for use in place of gasoline. A successful process was developed to make the methane from the carbon monoxide and hydrogen constituents of the gas.

The possibility of using methane as a motor fuel was recognized in Germany as early as 1935. At that time a test car was driven across Germany with a supply of methane carried in cylinders on the vehicle. The impurities in the gas used, however, caused difficulties, which yielded to further scientific work.

The war-developed process effects complete conversion of the carbon monoxide and carbon dioxide in the gas, together with part of the hydrogen, into methane and water. Impurities such as hydrogen sulfide, hydrogen cyanide, nitric acid and oxygen are completely removed. Organic sulfur compounds are reduced to traces. The process uses a nickel catalyst.

A complete report, made by post-war investigators, and published by the Office of Technical Services of the U. S. Department of Commerce, describes the pilot plant set up in Germany to manufacture the new motor fuel.

American improvements on the German coal-liquefaction process, which supplied the Nazi forces with much of their aviation and other fuels

during the war, give promise of gasoline and fuel oil at reasonable prices, Dr. H. H. Storch of the Bureau of Mines Pittsburgh laboratory recently told the American Chemical Society, Philadelphia section.

The German method of obtaining liquid fuels from coal is known as the Fischer-Tropsch process. It consists of the treatment of coal, or lignite, with steam to obtain water gas. The liquid fuels are made from this by combining the mixture of hydrogen and carbon monoxide in it by use of heat, catalysts, and sometimes pressure. Liquid fuels from natural gas are obtained by a similar process.

Several companies in the United States have done development work on a process utilizing what is known as the fluidized powder technique, Dr. Storch stated. In this a catalyst is used, a chemical that promotes the reaction without actually taking a chemical part in it. The catalyst in this process is ground to a fine powder and suspended as a cloud in the swirling gases.

During the past two years, the Bureau of Mines has developed a process which employs an ingenious new technique for removing the tremendous heat that is generated. An oil is introduced into the converter along with the gas mixture. As the oil touches the hot surfaces it evaporates and absorbs heat.

This technique permits elimination of bulky and expensive cooling equip-

ment, and at the same time affords excellent heat control. Also it permits the use of the catalyst in pellets. These are spread in a fixed bed. Compared with the fluidized powder technique,

## Burning Underground Coal

► PRODUCING GAS by burning unmined coal in the ground, in an experiment conducted early this year at Gorgas, Ala., by the Alabama Power Company and the U. S. Bureau of Mines, proved successful the Bureau has revealed. The underground residue, after the fire was put out, was examined by Bureau experts who now have prepared a report.

In this experiment, a U-shaped mine was developed in the coal bed, lying horizontally 30 feet under a hilltop, to form a pillar of solid coal 40 feet wide and 150 long inside the "U". It was completely separated from other coal in the seam. Burning was assisted by blasts of air, oxygen-air, oxygen-air-steam, oxygen-steam or steam.

By regular sampling and analysis of the gases given off, it was determined that the first three methods produced gas that could be used for generating power, while the last two

this process is much slower at its present stage of development, and requires more steel for installation. These disadvantages are expected to be overcome.

yielded gases suitable for manufacturing synthetic products.

At the end of the gas-making runs, which lasted about 50 days prior to the middle of March, the mine was cooled first with steam, then with water, to permit examination of the underground residue. About 236 tons of coal had been consumed completely, and 164 tons had been coked. The roof had not caved in during the burning process as had been expected, but had become plastic under the heat and expanded and settled down directly behind the coal face.

Of the five types of blast, air alone was used most frequently. For each pound of coal burned, this method produced an average of 108 cubic feet of gas.

The complete report on the experiment can be obtained from the U. S. Bureau of Mines.

## Superior Aviation Fuel

► MILITARY PLANES are now using an aviation fuel as much superior to 100-octane as premium grade motor gasoline is over regular grades, it has just been revealed. The new fuel is claimed to increase speed and range of planes from 12% to 15%.

This new super fuel, a petroleum product, is known as 115/145 grade. The present high-grade fuel known as 100-octane is 100/130 grade in

the industry. The new fuel was developed toward the end of the war and plans were made to use it in B-29s; that use did not materialize. However, oil companies are able to supply the fuel and nearly 2,000,000 barrels will have been delivered to the armed services early this year. The 115/145 grade fuel is harder to make because it requires a larger proportion of synthetic hydrocarbons.

## Fly in the Sugar Bowl Is Merely Refueling

# Carbohydrates for Flying Flies

► MAN FLIES on super-octane gasoline but the fly flies on sugar. When he lights on the sugar bowl, he is making a refueling stop.

Scientific evidence for this, which gives a basis of fact to the old saying, you can catch more flies with molasses than vinegar, was presented by Dr. Leigh Chadwick of the Army Chemical Center's medical division, Edgewood, Md., at the symposium on military physiology at the Army Medical Center.

The studies are part of a long range research program intended to provide basic information on the mechanism of action of poisons, such as insecticides, and perhaps to give leads to studies of the action of war gases.

Sweet stuffs and starches, scientifically known as carbohydrates, are the chief fuel foods and probably the only ones used by flies for the muscular activity of flying, Dr. Chadwick found.

Dr. Chadwick's study of flies started with earlier studies made of rattlesnakes. At that time he was making stroboscopic measurements of the speed of movement of the rattlesnake's tail and rattles. A good warm rattlesnake, he found, has the fastest movement of any vertebrate animal. It can beat its

tail at the rate of 100 vibrations per second. The speed of movement of the humming bird's wings, generally considered one of the fastest of such motions, is only 75 vibrations per second.

Fruit flies, the kind of flies he studied, beat their wings with a double vibration at a rate of 200 per second. This is the rate of contraction of opposing sets of muscles and is a very high degree of muscular activity. Wondering what sort of body metabolism, changing food to fuel and energy, made this possible, Dr. Chadwick set up experiments for measuring the oxygen consumption of fruit flies during flight.

The oxygen consumption of an animal or insect gives a measure of the kind of foodstuff used for fuel.

When flying, the fruit fly consumes 13 times as much oxygen on the average as he consumes when at rest. At the peak of flying, oxygen consumption goes up to 25 times that of the resting fly.

Some fruit flies, he discovered, can fly continuously for two or three hours.

After the fly has exhausted his supply of carbohydrate, he cannot fly, though he can stay alive another 24 hours. During this time he exists on fat, but he cannot fly on fat.

Spain normally exports most of the goat-hair obtained from its 6,000,000 goats and uses at home the hair from Spanish Morocco which is superior because of its coarseness and length.

Sumac has been used for tanning and dyeing since ancient times.

## New Chemical Drugs of Choice For Various Diseases

# Streptomycin, Penicillin or Sulfa?

by JANE STAFFORD

► IF YOU GET tularemia, or rabbit fever, your doctor will almost certainly give you streptomycin. But if you get typhoid fever, he will not give you streptomycin. And if you get a blood stream infection or blood poisoning from a hemolytic streptococcus germ, he will give you penicillin.

The average layman, having read much about streptomycin, the powerful mold remedy, is likely to expect his doctor to prescribe it for almost any ailment. The average physician may at times be perplexed over whether to give or not to give streptomycin. The reason for the physician's perplexity is that this remedy is so new its exact place as a medicine has not yet been completely determined.

To help the physician, the Journal of the American Medical Association has listed diseases and infections for which streptomycin is and is not good medicine.

The conditions for which streptomycin is effective almost all have long, unfamiliar names. It includes, besides tularemia, urinary tract infections, wound infections and bacteremias (blood stream infections) due to *Escherichia coli*, *Bacillus proteus*, *Pseudomonas aeruginosa*, and *Aerobacter aerogenes*; plague; meningitis due to all gram-negative bacilli; infections due to *Klebsiella pneumoniae*; and *Shigella dysenteriae*.

Streptomycin is reported occasionally effective, but penicillin is the drug of choice, in bacteremia and septicemia due to hemolytic streptococci; endocarditis (a kind of heart disease) due to green-producing streptococci; *Staphylococcus aureus* and *albus* infections; anthrax.

Penicillin is not the drug of choice for diphtheria. Streptomycin may be effective, but is powerless against the toxin, so anti-toxin should always be the primary treatment.

Streptomycin is partially effective but the extent of its usefulness is still undetermined in whooping cough, tuberculosis, leprosy and gonorrhea.

Streptomycin is generally not to be used at present in typhoid fever, paratyphoid fever, amebic dysentery, undulant fever, toxoplasmosis, histoplasmosis, acute rheumatic fever, disseminated lupus erythematosus, localized lupus erythematosus, infectious mononucleosis, pemphigus, acute and chronic leukemia, ulcerative colitis, coccidioidomycosis, malaria, poliomyelitis and all other virus infections, blastomycosis, moniliasis, and syphilis.

### Fights TB of Bones and Joints

► THERE WILL BE fewer crippled children in the future, fewer hunchbacks, fewer men and women limping through life on a stiffened or shortened leg, thanks to streptomycin.

Hailed as the first drug with real

usefulness in tuberculosis, this earth mold chemical is now being studied as a remedy for tuberculosis of the bones and joints which cripples so many children.

Doctors do not yet know whether it can do as good a job in this form of tuberculosis as it has in other forms of the great white plague.

"But there is reason to hope," says Dr. H. Corwin Hinshaw of the Mayo Clinic, "that streptomycin alone or in combination with surgery may be of considerable help in some of the most baffling problems in this field."

Scores of persons, many of them infants and young children, who would have died two years ago of tuberculous meningitis or of another previously always fatal disease, miliary (not military) tuberculosis, are alive and well today and "may be regarded as cured," he said.

Streptomycin has not cured all patients with this form of the disease, which kills thousands annually. But it is the only effective remedy.

The earth mold chemical has been effective very promptly and in a very high percentage of cases of another form of tuberculosis. This is the dreaded and painful type which involves the larynx and vocal cords. A somewhat similar type of tuberculosis may produce ulcers in the windpipe and larger bronchial tubes. This type which has been so hard to cure by other forms of treatment responds very well to streptomycin.

Tuberculosis of the lungs accounts for more than 90% of tuberculosis deaths. This type of the disease is a destructive process, and lung tissue which has been destroyed cannot be

regenerated. But there "is no longer any doubt," Dr. Hinshaw said, "that streptomycin has very great value in some of the most fulminating types of lung tuberculosis."

Streptomycin is not the only treatment for tuberculosis. Just as the pneumonia patient who gets penicillin treatment must go to bed and be given other helpful remedies, the tuberculosis patient who gets streptomycin will need to rest in bed and get other forms of treatment as well as the mold drug. And like the pneumonia patient cured by penicillin, the tuberculosis patient who gets streptomycin also needs to be guarded during the convalescent period.

Speaking at the presentation to Merck and Company of the biennial award for chemical engineering achievement given by Chemical Engineering, McGraw-Hill publication, Dr. Hinshaw observed that two and three years ago anything said or written about streptomycin had to be guarded because scientists then feared that streptomycin would never be made in sufficient quantity or at a low enough price to make it available to the hundreds of thousands suffering with tuberculosis. The one gram a day considered enough in many types of tuberculosis now costs only a few dollars.

#### **Chemical Reinforces Penicillin**

► PATIENTS with the heart disease, sub-acute bacterial endocarditis, have a better chance of being cured, thanks to a new chemical that keeps penicillin in the blood longer. The chemical is called caronamide and was developed by Dr. K. H. Beyer, of Sharp and Dohme.

It is effective in keeping high levels of penicillin in the blood of patients where excessively high levels are necessary for cure.

Besides enhancing the curative possibilities of penicillin for these patients, caronamide helps to conserve the consumption of the mold chemical, thereby lessening the cost of treatment. In cases requiring such huge amounts of penicillin, this is a matter of some importance.

#### **Tyrothricin for Scabies**

Tyrothricin, one of penicillin's cousins among the new antibiotic

remedies, has now been used successfully to treat scabies, or the itch, in cases complicated by a secondary infection with pus formation.

Within two weeks active sores disappeared in 69 out of 71 cases, reported by Drs. Harry M. Robinson and Harry M. Robinson, Jr., of the University of Maryland School of Medicine.

The tyrothricin, which is an anti-germ chemical from a soil bacillus, was used in a mixture with benzyl benzoate, standard scabies remedy. Only one moderately severe reaction to the tyrothricin occurred.

### *Penicillin-Like Drug from Saliva*

► FUTURE SUPPLIES of a penicillin-like antibiotic drug may come from a germ found in human saliva if practical development can be made from a discovery reported by Dr. Richard Thompson and Madoka Shibuya of the University of Colorado School of Medicine to the Society of American Bacteriologists.

Green streptococci, ordinarily harmless germs, produce a substance that stops diphtheria germs from growing in the test tube. The presence of the streptococci in the mouth probably would not give protection against diphtheria since there are other substances in saliva that interfere with the antibiotic action.

If the material can be obtained from

the saliva organisms, however, it might become another antibiotic remedy. That is a problem for future work, Dr. Thompson said.

Clue to the saliva antibiotic came from a German report of a germ-checking substance they had found in saliva and called inhibine. They thought it was like lysozyme, an anti-germ chemical in saliva, tears and other body fluids, discovered by Sir Alexander Fleming years before he discovered penicillin.

The Colorado workers, following the German lead, were investigating saliva, trying to learn more about this germ-checking action, when they stumbled on the fact that it was the green streptococci in the saliva that were producing it.

Rutin, a little known glucoside drug obtained from certain types of tobacco, is used in the treatment of a tendency to hemorrhage; a new and improved process for its extraction has been developed.

## For the Home Lab

### Selenium

by BURTON L. HAWK

► FOR THOSE who like to wander off the beaten path and venture into the more unfamiliar fields, we propose to include in this series of articles occasional experiments with the lesser known elements or the so-called "rare" elements. These are the elements which are included in most textbooks under the heading, "Some Other Elements," or "Miscellaneous Elements." Very rarely does the chemistry class study about them in detail, if at all. As a result, we find that the majority of chemistry enthusiasts know very little concerning their properties.

Let us begin our investigation of these elements with selenium, a member of the sulfur family.

#### The Element

Selenium can be purchased at most chemical supply houses. It is priced about the same as magnesium, and using only small quantities will not make the cost prohibitive. One ounce should be sufficient for the experiments mentioned herein.

Like sulfur, selenium exists in several allotropic forms.

**Metallic:** This is the form in which selenium is usually supplied commercially, either as lustrous, metal-like sticks or as a dark gray powder. Although termed "metallic," it must be remembered that selenium is a non-metal (sulfur family). If you can obtain selenium as a powder, sift a small quantity of it into an open flame. It

burns brilliantly with a bright blue flame forming the dioxide which, true to the sulfur family tradition, has a disagreeable odor resembling rotten radishes, of all things! You can melt the powdered selenium into a coherent metal-like mass by placing in a porcelain evaporating dish and heating. This form of selenium is insoluble in carbon disulfide.

**Vitreous:** If you melt selenium in an evaporating dish and quickly pour the molten mass into a beaker of cold water, a brittle, dark brown or black mass will be obtained. This is still selenium in another form, and still insoluble in carbon disulfide.

**Amorphous:** This is a dark red powder so different from the metallic variety that it is hard to believe it is the same substance. We will prepare it later on. Incidentally, it is soluble in carbon disulfide.

**Colloidal:** Obtained as a dark red powder. It dissolves in water forming a red fluorescent solution.

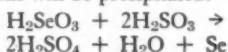
**Crystalline:** Dark red, brown or black crystalline powder.

#### Selenium Dioxide, $\text{SeO}_2$

Unlike sulfur, the oxide of selenium is not a gas but a solid. Usually it is obtained in the form of a white crystalline powder. Dilute about 2cc. of nitric acid with an equal quantity of water. Add a small amount of selenium and heat until it is entirely dissolved. The selenium is oxidized by the nitric acid forming a solution of

selenous acid,  $H_2SeO_3$ . To obtain the dioxide, evaporate the solution to dryness. The powder remaining has the typical selenium-odor of radishes.

Now prepare selenous acid again by dissolving a portion of the  $SeO_2$  in hot water. If sulfurous acid be added to this solution, the red variety of selenium will be precipitated:



The precipitate formed is at first yellow, then gradually darkens through various shades of orange to brick red. The sulfurous acid for this reaction may be prepared by adding sodium sulfite or bisulfite to a dilute solution of hydrochloric acid.

Hydrogen sulfide will precipitate both sulfur and selenium from selenous acid. Dissolve another portion of the solid dioxide in water. You can either bubble hydrogen sulfide through this solution or add a solution of sodium sulfide and avoid the disagreeable odor of  $H_2S$ . The yellow precipitate formed will turn red upon heating.

### Hydrogen Selenide, $H_2Se$

Hydrogen forms with selenium a colorless gas with an odor of rotten horseradish. It is more toxic than  $H_2S$ , and must not be inhaled. It is prepared by adding dilute hydrochloric acid to ferrous selenide. The ferrous selenide is formed by heating together equal quantities of iron filings and powdered selenium. Lead the  $H_2Se$  into a solution of sodium sulfite and

Ethyl alcohol, a basic organic raw material, is used in larger quantities in making synthetic rubber than in all other uses added together.

Dairy cows should have one pound of grain for each  $1\frac{1}{2}$  to two quarts of milk produced.

a mixture of sulfur and selenium is precipitated. Selenides are formed by leading the gas into solutions of salts of the metals. Try preparing the selenides of lead, silver, copper, nickel, etc. Hydrogen selenide will burn when ignited and will dissolve in water, similar to  $H_2S$ .

### Other Compounds

No trioxide of selenium is known. Selenic acid,  $H_2SeO_4$ , white, hygroscopic crystals, dissolves in water forming a corrosive, acid liquid. It is formed in solution by oxidizing silver selenite with bromine.

Selenium oxychloride,  $SeOCl_2$ , is a very active and corrosive liquid attacking many metals.

### Uses

The metallic variety of selenium has a very unusual property. It is a fair conductor of electricity; however, this conductivity is greatly increased by light. Perhaps you can set up some arrangement in the home lab to demonstrate this property. This peculiar characteristic of selenium is utilized in photoelectric cells and photometers. Added to glass in minute quantities, it imparts a ruby color familiar in the tail-light lenses of automobiles. It is also used, similar to sulfur, in vulcanizing rubber.

Selenium is obtained as a by-product during the refining of copper. It is not produced in any quantity because the demand for it is small. Perhaps some day some one will find a greater use for it.

New Materials Join Old Principles  
To Furnish New Crop of Inventions

## Patents With Chemical Angles

*To obtain copies of patent specifications send 25 cents in currency, money order or Patent Office coupon for each and order by number from the U.S. Commissioner of Patents, Washington 25, D.C.*

### "Hydrophobic" DDT Powder

► MOSQUITO "wrigglers" coming to the surface to breathe, also their mothers coming down to lay another clutch of eggs, are in for worse DDT trouble than ever. For covering the water surface there is very likely to be a persistent, poisonous film of a new "hydrophobic" DDT.

This does not mean that the mosquitoes will get hydrophobia; it merely means that the etymology of this new entomological woe indicates that the compound "hates water," in the sense that it cannot be wetted and thus washed out or sunk.

This new, unwettable form of DDT, on which U.S. patent 2,430,288 has been issued to a duPont chemist, Albert L. Flenner of Wilmington, Del., is prepared by hooking the DDT molecules up to molecules of stearylamine, which are long-tailed affairs built somewhat like soap molecules, then mixing to a paste with tricalcium phosphate. Dried and re-powdered, this forms highly fluid dust, the particles of which stick to each other but will not stick to water. Hence their excellent film-forming properties.

### New Jobs For Magnetism

► THE MAGNET's attraction for iron and related metals is put to new uses in two patents, 2,430,157 and 2,430,167.

The first, awarded to W. Byrd, Jr., of Princeton, N.J., is a device for the removal of iron and steel particles from oil and other liquids where they might do harm. The liquid is passed through a filter, which is placed within the hollow core of an electromagnet. A handful of ordinary carpet tacks provides additional magnetic points for the picking up of the small bits of metal.

The second invention, developed by Raymond L. Fitch, Pacific Palisades, Calif., is a machine for inspecting small metal objects by means of their magnetic properties. Flawed pieces are automatically thrown out.

Related to this, but utilizing differences in electrical conductivity instead of magnetic responses, is the invention of Warren S. Reynolds of Stratford, Conn., on which patent 2,430,080 has been awarded. It is intended especially for the sorting of the small copper cups in which cartridge primers are contained. Patent rights have been assigned to the Remington Arms Company.

### Wax From Sugar Cane

► WAX RESIDUES in sugar cane wastes, until now thrown away, are salvaged through the process on which W. F. Goepfert of Short Hills, N.J., has obtained patent 2,430,012. The waste is

digested with a solvent, isopropyl acetate, then filtered, and the filtrate allowed to cool. As it cools the waste precipitates out.

### Taming PETN

► A NEW WAY of taming the terrifically violent and "touchy" explosive, pentaerythritol tetranitrate, is offered by a Swiss chemist, Hans Mueller of Othmarsingen, for patent 2,430,239. During the war, this explosive was slowed down by the addition of TNT; Herr Mueller states that pentaerythritol stearate and dinitrobenzene are more effective.

### Powdered Coal

► VERY FINELY powdered coal, for enriching oil fuels used in industrial power plants, is prepared by an improved process on which patent 2,430,085 has been issued to two Kansas engineers, K. A. Spencer and D. W. Machin. The broken coal is washed, dried by heat, put first through a crusher, then through a ball mill. To diminish danger from dust explosion, dust coming off in the drier is sucked out by an exhaust draft, electrically precipitated, and added to the final product.

### Powder Fire-Extinguisher

► A FIRE-EXTINGUISHER that puts out fires with a dry powder instead of wet liquids or clinging foam is presented by Michael E. Keefe, Jr., and Ida K. Keefe of Atlanta, for patent 2,430,470. The principal container holds a charge of finely pulverized sodium bicarbonate, which on contact with heat releases fire-smothering carbon dioxide. Propellant power is furnished by a cylinder of carbon dioxide under high pressure, which of course adds to the fire-killing capacity of the device.

### Balloon Cloth

► A NEW light-weight fabric, suitable for balloons because it has the necessary strength and the ability to hold gas without leakage, is composed of a continuous plastic sheet of a vinylidene chloride and vinyl ester cemented to woven fabric of resin fibers with a vinyl chloride adhesive. The patent was assigned to Wingfoot Corporation, Akron, Ohio, by the patentees, Oscar W. Loudenslager and Joseph E. Wilson of the same city. The number is 2,431,056.

### Measuring Dissolved Oxygen

► PHOTOMETRIC APPARATUS for the continuous determination of dissolved oxygen in water, was awarded patent 2,430,895. The recipients were Richard L. Tuve, Silver Spring, Md., Joseph C. White, University Park, Md., and Elmer M. Luke, Washington, D.C. Its practical application is with steam generators. Due to the corrosive properties of dissolved oxygen in water used in these generators, it is highly important to be able to determine the oxygen concentration. This apparatus gives a continuous analysis system.

### Spray-Molded Chinaware

► A NEW WRINKLE in one of the world's oldest crafts, the making of pottery, won patent 2,431,629 for two Los Angeles inventors, F. V. Wind and M. J. Raimondo. Instead of turning the clay mass on a potter's wheel or pressing it in a mold, the new process sprays a highly fluid suspension against the walls of a porous mold.

Spray and mold are given opposite electrostatic charges, so that the droplets stick and coalesce into a continuous mass, while the porosity of the mold sucks out the water, leaving the

mix of the proper consistency for drying and firing. The inventors have assigned their patent rights to Pacific Clay Products, a California corporation.

#### **Competition For Tapioca**

► **WAXY-ENDOSPERM** corn and sorghum, which replaced tapioca as the source of "stickum" for envelope flaps and postage stamps when war cut off our former imports, now promise to

take over tapioca's role as dessert, too. Herman H. Schopmeyer of Hammond, Ind., has obtained patent 2,431,512 on a method of preparing starch from these native crops to form the sticky, slippery granules which some persons like. The starch is first made into a dough with water, then heated to between 220 and 250 degrees Fahrenheit and stirred until it forms pellets. Patent rights are assigned to the American Maize-Products Company.

### *Fog-Foam Firefighting on Ships*

► **FOG-FOAM FIREFIGHTING** systems are being installed on a number of Navy aircraft carriers and firefighting tugs. They are expected to reduce greatly the danger from gasoline fires aboard ships.

Gasoline fires are hard to extinguish by ordinary firefighting methods. The use of fog-foam, instead of water, has been found successful. The foam is a smothering mass of snowy bubbles which lasts for hours and can be spread several inches thick by use of special nozzles to seal inflammable gases and keep oxygen out.

This mechanical foam is made from soybeans, fish scales and iron salts. It is carried aboard ship in special containers but is mixed with water in use. Its adhesive qualities make it

stick to anything; a gale will not blow it away, and it can be laid in dikes to confine a gasoline fire.

A special nozzle developed for the Navy can be adjusted to throw a solid stream or to send the water through jets to produce a fine mist-like spray. The advantages of fog lie in its superior heat absorption, its use of small quantities of water, protection of firefighters from heat, and reduced water damage.

A further use of mechanical foam is in fighting above-the-ground oil tank fires. The foam is pumped into the tank through the oil pumping line itself at the bottom of the tank, rises through the oil, cools the oil below ignition temperature, and kills the fire. In this application the foam cools rather than smothers the fire.

While natural gas and petroleum are found together and much of the gas supply is obtained from wells yielding both, the greater part is from wells which contain gas only.

The Union of South Africa is pushing a program of supplying food yeast cheaply enough so that it can be included in the diet of all classes; the raw material for its production is domestic molasses.

## Americans Save Food For Germans

► ONE HUNDRED and twenty thousand tons of fruits and vegetables from German gardens that otherwise would have been wasted were saved for use this winter, thanks to researches by scientists at the U. S. Bureau of Human Nutrition and Home Economics here.

The vegetable saving was accomplished through efforts of Dr. Esther Batchelder of the Bureau while on an Army mission to Germany last summer. She went, with Miss Jane Ebbs of the Office of the Quartermaster General, and Dr. Helen Oldham, of the University of Chicago, primarily to teach Germans how to use corn for food. Neither the Germans nor the British, in whose zone most of the corn had landed, were familiar with its use as human food.

It was dried corn that had been shipped, to relieve the shortage of wheat and other grains. Dr. Batchelder expected to find the trouble largely a matter of distaste for cornmeal. Instead, she found that the Germans were trying to mill the corn like wheat. This was "beating the life out of their wheat mills" and producing a gritty, unpleasant meal from which most of the nourishing starch had been sifted and discarded. So she and her companions had to visit all the states in the British and American zones, telling German millers and British and American military authorities how to grind corn into meal. Then they got out a bulletin for housewives, telling them of the nourishing value of cornmeal and giving recipes for making cornbread and other cornmeal dishes.

In the course of this work, she found that the Germans who were not farmers but had been given small garden allotments had surplus fruits and vegetables which were going to waste for lack of means of preserving them. This was serious, not only because of the over-all food shortage but because those with garden allotments could not get fruits and vegetables on their food rations.

Dehydration, or drying, seemed the answer, but there were no dehydrators in Germany, and the ovens of the kitchen ranges in most of the homes were so small they could not be used satisfactorily for drying vegetables. So, with the aid of a competent German woman and two technicians and laboratory facilities at Heidelberg University, Dr. Batchelder worked out a dehydration method suitable for German housewives.

The drying trays were made of wooden sticks used to tie up tomato vines. They were tied together with an ersatz string, because there were no nails. They were covered with whatever cloth was at hand. And they were made in sizes suitable for stacking over small electric hot plates, like those used for coffee makers in the United States. Most of the homes that had small gardens had these electric plates. The dehydrator racks were left without walls, so that air could help in the drying process.

The figure on the saving in fruits and vegetables through these dehydrators was reported to the Bureau by military government officials after Dr. Batchelder's return.



## New Use for Gold

► MERCURY, made from gold in the atomic pile by neutron bombardment, has now been obtained in large enough quantities to perfect methods of measurement by the most precise standard of length yet devised. This unit is a single wave of green light from mercury with an atomic weight of 198.

Research laboratories for a number of years have been using light waves for special types of length measurements, but the use of this isotope provides precision not available before. The National Bureau of Standards,

which now has Mercury 198 in reasonable quantities and has developed practical methods for its use in measurements, states that the discovery makes possible an "ultimate standard of length." The legal standard is a meter bar kept in the vaults of the Bureau.

University of California scientists announced the process a year ago. It was by means of a cyclotron at the university that gold was transmuted to Mercury 198. Quantities obtained were very small. The Bureau's work, carried out by Dr. William F. Meg-

gers, is a refinement of other processes plus the development of mercury lamps and measuring procedures.

Measurements based on this mercury green light wave, which is 21 millionths of an inch long, will make possible length determinations precise to one part in 100 million. Such precision in the measurement of length has never before been attained by man, Dr. E. U. Condon, director of the Bureau, declares.

The advantages of a light-wave standard over a physical standard are that it is indestructible and exactly reproducible, and that any laboratory with the necessary auxiliary equipment can have a basic standard on the premises.

Cadmium red radiation was adopted provisionally at the 1927 International Conference on Weights and Measures as a wavelength standard. The fundamental advantage of Mercury 198 over cadmium is that it emits a more nearly

perfect monochromatic light. By this is meant that the red, green, or other color used, is a single wave-length rather than multiple wavelengths extremely close together.

Cadmium consists of six principal isotopes that radiate slightly different waves. Other advantages of mercury are that it does not need special heating equipment as does cadmium, and that the human eye is seven times more sensitive to green light than to red.

Dr. Meggers is now experimenting with a number of lamps for using the mercury. The simplest is a glass tube the size of a cigarette with Mercury 198 sealed inside it. When excited by high-frequency radio waves, the mercury glows and gives off energy in the form of light. The Bureau expects at a later date to have lamps of this sort available for other scientific laboratories.

## Magnesium Alloy Uses

► MAGNESIUM ALLOY castings are achieving many uses, ranging from aircraft to household devices, because of their lightness and strength, the American Society of Mechanical Engineers was told recently by A. W. Winston and M. E. Brooks of the Dow Chemical Company, Midland, Mich.

These alloys, they said, are distinguished for their low weight, high strength, easy machinability and other desirable properties. They can be fabricated by any of the commonly used foundry methods, such as green sand, dry sand, plaster, permanent mold, and die casting.

In common with most other pure metals, pure magnesium ordinarily is not considered as a structural material, the Dow scientists said. When alloyed with suitable amounts of aluminum, zinc, and manganese, the properties of the alloys are comparable with those of the aluminum alloys. The total of added metals is usually about 10%.

Melting of magnesium alloys usually is done with flux protection to prevent oxidation of the molten metal by air. This means the use of a chemical to form a gas to keep the oxygen of the air away from the heated metal.

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ISTRY

## Frivolous Effervescence and Caustic Comment

by OUR READERS

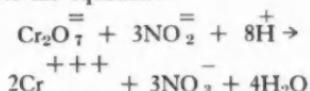
► "I AM READING my second number of CHEMISTRY tonight—it is really swell—just what I have always been looking for. I would like very much to have suggestions about chemical shows and demonstrations in the magazine—sounds interesting."

Miss N. McC., Macedonia, Iowa.

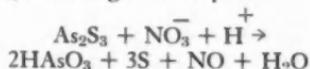
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► "IN REFERENCE to Miss R. M. B.'s article on removing N and NO<sub>2</sub> compounds from a lithium carbonate solution, I would like to offer a suggestion as to my idea of separating them.

The N and NO<sub>2</sub> compounds can be oxidized to NO<sub>3</sub> compounds according to the equation:



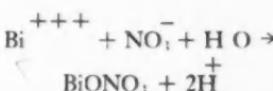
This reaction must be carried out in acid solution. Having the nitrogen compounds thus converted to nitrates, the nitrates are reduced to NO gas by As<sub>2</sub>S<sub>3</sub> according to the equation:



This reaction must also be carried out in acid solution. Thus the N and NO<sub>2</sub> compounds pass off as NO gas.

The nitrates can also be precipitated with bismuth ions if this ex-

cise is one of precipitation. The nitrates hydrolyze forming an insoluble compound:



This reaction is readily reversible, and therefore an excess of hydrogen ions should be avoided to keep the insoluble BiONO<sub>3</sub> from redissolving."

C.G.S. Chicago, Ill.

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► R. C., JACKSON HEIGHTS, N. Y., sends a "caustic comment" about Miss R.M.B.'s efforts to remove impurities from lithium carbonate: "Remove .03% Cl with AgNO<sub>3</sub>? I double dare her! First, why do you want to remove .03% Cl? Second, the silver chloride formed is soluble to the extent of .000089 grams per 100 cc of sol. How will she remove this if she wants such accuracy? In 100 cc of water about 1.281 grams of lithium carbonate will dissolve. In this 100 cc therefore there is .27% of the silver chloride left in solution. Ha! What will she do with the silver carbonate that will form? This is even more soluble than silver chloride, so how can the silver be removed? . . . if this C.P. chemical *must* be made even more C.P., I have only one suggestion. Buy a mass-spectrograph and separate it that way!"

## How Solid, Liquid and Gas Change Places Predictably

# Components and Phases

A Classic of Chemistry

*Reintroduced to American chemists by their own Dr. Bancroft, the Phase Rule developed from the laws of thermodynamics as worked out by Josiah Willard Gibbs. The fundamental reference for Gibbs' publication is Vol. 3, Trans. Conn. Acad. The Theorem of Le Chatelier appeared in Comptes Rendus 99:786 (1844). Further application of these principles to chemical problems was carried out in Europe, and the trail of references winds through various European journals of the time, especially Recueil Trav. Pays-Bas.*

THE PHASE RULE, by Wilder D. Bancroft. *The Journal of Physical Chemistry, Ithaca, N. Y. 1897.*

► THE TWO EXPRESSIONS describing in a qualitative manner all states and changes of equilibrium are the Phase Rule and the Theorem of Le Chatelier. A phase is defined as a mass chemically and physically homogeneous or as a mass of uniform concentration, the number of phases in a system being the number of different homogeneous masses or the number of masses of different concentration. In the case of water in equilibrium with its own vapor there is the liquid and the vapor phase, two in number. If there is a salt dissolved in the water there are still two phases, the liquid or solution phase and the vapor phase. If ice crystallizes, there is added a

solid phase and the number becomes three. If, in addition, the dissolved substance separates in the solid form or as a second liquid layer, there will be four phases present, the vapor, liquid and two solid phases or the vapor, solid and two liquid phases as the case may be. Although the ice separates in many crystals, yet each is like every other in composition and density and taken together they constitute one phase. If the crystals were not alike as is the case with rhombic and monoclinic sulfur they would form as many phases as there were kinds of crystals, two in the example just cited, three if we have diamond, graphite and carbon. The components of a phase or system are defined as the substances of independently variable concentration in the phase or system under consideration. A component need not be a chemical compound, that is a substance described by the Theorem of Definite and Multiple Proportions, though this is usually the case. For instance, a mixture of propyl alcohol and water in such proportions that the percentage composition of the liquid is the same as that of the vapor might be treated as one component; but there is no advantage in this, as it is true for only one temperature and when there are no other components. The main point to be observed in determining the number of components in a given

system is that each compound is not necessarily a component. Thus a hydrated salt is to be treated, when in equilibrium with the solution or vapor, as made up of salt and water and is not in itself a component. The same holds true of a double salt such as the double sulfates of copper and potassium. Here the components are the two single salts and water because the concentration of these three can be varied and they are sufficient to form all modifications which can exist. If one is treating calcium carbonate in equilibrium with calcium oxide and carbonic acid, there are only two components, calcium oxide and carbonic acid; for the calcium carbonate is merely a solid phase containing the two components. The fact that the two components unite to form a phase in definite proportions does not have anything to do with the matter. On the other hand it is not permissible to take calcium and oxygen as two of the actual components of this system because they are neither independent variables nor are they in equilibrium with the system.

It has been shown by Gibbs that the state of a phase is completely determined if the pressure and temperature together with the chemical potentials of its components be known. There is therefore an equation connecting these quantities which will describe the phase. For each other phase in equilibrium with the first there will be another equation containing the same variables.

There will thus be the same number of equations as there are phases, while the number of independent variables will equal the number of components plus the temperature and

pressure. If the number of components be " $n$ " the number of variables will be " $n + 2$ ." This is true only in case we are considering a system uninfluenced by gravity, electricity, distortion of the solid masses or capillary tensions because it is only when the effects due to these influences are removed that the values for the pressure, temperature and chemical potentials are uniform throughout the whole system. While we do not know the single equations referred to nor the chemical potentials of the components, it is possible to draw some conclusions in respect to the possible number of states of equilibrium in any given case. Since the number of independent variables is always equal to " $n + 2$ " by definition and the number of equations equals the number of phases, it follows that in a system of " $n + 2$ " phases there will be as many theoretical equations as there are variables; in other words, that each of the variables has one value and one only for a given set of " $n + 2$ " phases. A given combination of " $n + 2$ " phases can exist at one temperature and one pressure only, the composition of the phases being also definitely determined. Such a system is called a nonvariant system, the temperature and pressure at which alone it can exist are known as the inversion temperature and pressure. If there are only " $n + 1$ " phases, the system is no longer completely defined and has one degree of freedom. It is therefore called a monovariant system. If we fix arbitrarily one of the variables, say the pressure or the temperature, the system is again entirely defined. The characteristics of the monovariant system are that for a

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given combination of phases there is for each temperature one pressure and one set of concentrations for which the system is in equilibrium; for each pressure, one temperature and one set of concentrations; for each set of concentrations, one pressure and one temperature. A system composed of " $n$ " phases is called a divariant system. In it there are two variables which can be fixed arbitrarily before the system is completely defined. In such a system, for a given temperature, it is possible to have a series of pressures by changing the concentrations or a series of concentrations by changing the pressures. For a given pressure the temperatures can vary with changing concentrations and *vice-versa* while for definite concentrations there are similar relations between the pressures and temperatures. If instead of " $n$ " phases the system contains  $n-1$ ,  $n-2$ , etc., phases it is known as a trivariant, tetravariant system, etc. There are other terms in use, a monovariant system being called a "case of complete heterogeneous equilibrium" while a divariant system is known as a case of "incomplete heterogeneous equilibrium." These phrases are unwieldy and unsatisfactory and must give way to the more rational nomenclature adopted here.

By increasing the number of components and decreasing the number of phases it is possible to make a system with almost any degree of freedom; but, practically, a system ceases to be interesting from the qualitative point of view when it contains less than " $n$ " phases because the possibilities are so numerous and so ill-defined. In the other direction, that of decreasing the components and increasing

the phases, it is impossible to go. Since " $n+2$ " phases constitute a nonvariant system which can be in equilibrium at one temperature and pressure only, a system of " $n+3$ " phases is most improbable and none such are known where there are no so-called passive resistances to change. The discussion will therefore be limited to nonvariant, monovariant and divariant systems, starting with the number of components equal to one and increasing to four. Before beginning the study of the possible variations in equilibrium caused by changing the different variables and the number of phases, it is necessary to have some clue as to the direction of the change in equilibrium when there is an alteration in the system. This is given by the Theorem of Le Chatelier, which says: "Any change in the factors of equilibrium from outside is followed by a reverse change within the system." If the external pressure is raised there is an increased formation of the component or phase occupying the lesser volume; if heat is added there is increased formation of the component or phase involving an absorption of heat; if the concentration of one component is increased in a given phase there is formation of the component or phase which involves a decrease in the concentration of the first component. In other words, the system in equilibrium tends to return to equilibrium by elimination of the disturbing element. It is now possible to take up distinct cases and see the way in which the Phase Rule and the Theorem of Le Chatelier apply. It must be borne in mind that we are discussing only the states and changes of equilibrium which are due

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to the pressure, temperature and concentrations, and that the disturbing effects due to gravity, electricity, distortion of the solid masses and capillary tensions are eliminated. If this is the case the problem becomes simplified since the absolute mass of the phase has no effect on the equilibrium, because the concentration of a phase is not a function of its mass. A saturated solution remains saturated whether it is in contact with a small or a large amount of the solid. In the same way the equilibrium is not disturbed if the bulk of the solution be poured off. This would not be true if we were taking into account the effect due to gravity. Crystals at the bottom of a long tube filled with solution are under a greater pressure than if the liquid layer were but a few millimeters thick; and have different solubilities in the two cases. This is very noticeable in divariant systems of three components when there is a vapor phase in equilibrium with two liquid phases. An increase in the amount of the upper liquid layer produces a very distinct change in the mass of the lower liquid phase. This is a point which has been completely overlooked

in the development of Nernst's Distribution Theorem. The pressure of a gas in a tall cylinder is not strictly uniform owing to the influence of gravity. These effects as a rule are very small and may be neglected in most cases without danger. They can be reduced to a minimum by working with small quantities.

It will be noticed further that the classification of equilibria under the Phase Rule and of changes of equilibria under the Theorem of Le Chatelier is perfectly general and involves no assumptions as to the nature of matter or of the changes taking place. There is no need of assuming that matter is made up of discrete particles nor that it is continuous; there is even no need of assuming its existence or non-existence. It is immaterial whether there is or is not a distinction between "chemical" and "physical" reactions. It is simply a question of the relative number of independently variable components and phases in the one case and of the experimental data in regard to heat effects, densities and concentrations in the other.

## One Component

The most familiar example of a nonvariant system made up of one component is the equilibrium between solid, liquid and vapor, as in the system composed of ice, water and water vapor, or solid, melted and vaporized naphthalene. The application of the Phase Rule leads us to expect that a system of this type can be in equilibrium at only one temperature and one pressure. This is

true experimentally, the temperature for water being about zero degrees Centigrade and the pressure about four and a half millimeters of mercury. In the ordinary determinations of the inversion temperature in open vessels there are really two components instead of one, the substance under consideration and air, so that the values cited for water are not the temperature and pressure at

which the three modifications of water would be in equilibrium if they alone were present. The effect of the air in changing the inversion temperature is due to its solubility and also to its pressure upon the solid and liquid phases. Since the effect of a pressure of one atmosphere is very slight and since the amount of air dissolved in water is not usually very great, the value of the inversion temperature as found in open vessels differs only slightly from the true value and for purposes of discussion the two may be considered identical in most cases. This is especially true if the determination is made by melting the solid in presence of its own vapor instead of freezing the liquid. In the table are the inversion temperatures and pressures of several substances. The first column of figures gives the temperature in Centigrade degrees; the second, the pressure in millimeters of mercury:

	Temperature	Pressure
Bromine	-7.0°C.	44.5 mm.
Ice	0.0	4.6
Benzene	5.3	35.4
Acetic acid	16.4	9.4
Naphthalene	79.2	9.
Iodine	114.2	90.
Camphor	175.	354.

If we start from any system in equilibrium it is possible, by adding or subtracting work or heat, to bring about changes in the relative masses of the phases and, under suitable conditions, the disappearance of one or more phases. The direction of these changes can be predicted from the Theorem of Le Chatelier if we know the densities and concentrations of the different phases and the sign of the heat effect when one phase increases at the expense of one of the others. The vapor of a substance is less dense than the liquid or solid modification at any temperature at which it can be in equilibrium with either of these.\* The vapor of a substance is less dense than the liquid or solid modification. Increase of external pressure means therefore decrease of the vapor phase and *vice-versa*. Some substances are more and some are less dense in the solid than in the liquid state so that it is necessary to know the peculiarities of the system under consideration in order to tell which of these two phases is the more stable under increased pressure. The change of solid into liquid and of liquid into vapor always involves absorption of heat.

## Two Components

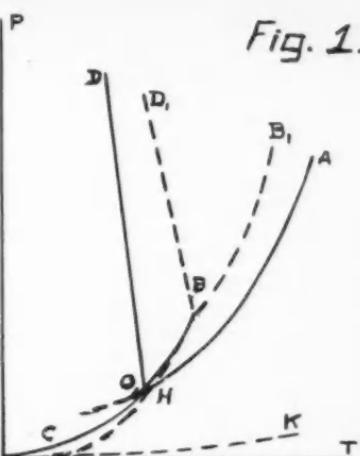
A phase consisting of two or more components is called a compound if it is described by the Theorem of Definite and Multiple Proportions, a solution if this is not the case. A solution may also be defined as a phase in which the relative quantities can vary continuously within certain

limits or as a phase of continuously varying concentration. This definition does not confine solutions to the liquid phase, but includes mixtures of gases and of solids. . . .

\* This would not be true for supercooled vapor near the critical temperature; but it holds for all cases of stable equilibrium.

When there are two components it requires four coexisting phases to constitute a nonvariant system, three and two for a monovariant and a divariant system respectively. Since no two components exhibit all the types of equilibrium, it will be better to consider a series of characteristic pairs, each illustrating some new case of equilibrium at an easily accessible temperature and pressure. It will then be possible to classify the different phenomena so as to gain a view of the whole field. Having studied in detail the effect of changes of external pressure and temperature on a system of one component it will not be necessary to repeat this when there are more components unless there is some new feature introduced thereby. The first case to consider is the one where the two components do not crystallize together, exist each in only one solid modification, and there is only one nonvariant system possible at ordinary temperature, two solid phases, solution and vapor. The equilibrium between potassium chloride and water will serve as a type. The graphical representation of this system with the pressure and temperature as co-ordinates is given approximately in Fig. 1.

The nonvariant system, potassium chloride, ice, solution and vapor, is found to be possible experimentally at one temperature and one pressure only, represented in the pressure-temperature diagram by the point O. Any continued change in the external conditions produces finally the disappearance of one of the phases, the temperature and pressure remaining constant so long as all four are present. Which of the two solid phases



► THE DIVIDING LINE between solid and liquid shifts with increase of temperature (T) and pressure (P) along the curve OA. In this diagram, the line shows the conditions under which a saturated solution of potassium chloride in water can exist. OB is the corresponding curve for the solid solvent. O is the freezing point. OC shows the conditions under which there is equilibrium between ice, solid potassium chloride and vapor. Equilibrium between salt, ice and solution follows the curve OD. Any change in external pressure produces a change in the quantity of one of the phases, and for each temperature there is but one pressure at which the system can exist. Dotted lines are special cases.

disappears first on addition of heat depends on the relative quantities of the two, and if present in the same proportion as in the solution they will disappear simultaneously. In this case the whole of the solid will melt or the whole of the solution will freeze

without change of temperature, a behavior which is often assumed erroneously to be a criterion of the purity of a compound. . . .

If solid salt be present in excess, the ice will be the first phase to disappear on addition of heat, leaving the monovariant system, salt, solution and vapor. For each temperature there will be a definite pressure in the vapor phase and a definite concentration in the solution at which the system can be in equilibrium and this pressure and this concentration will vary with the temperature. In the diagram, the curve OA represents the pressures and temperatures at which the saturated solution can exist. It is a solubility curve, water being the solvent. Addition of liquid to the solution from outside or from the vapor phase by condensation causes more of the salt to go into solution until the equilibrium concentration is restored; removal of water, by evaporation for instance, brings about a precipitation of the solute. Both these changes are in accordance with the Theorem of Le Chatelier. Addition of water means a decrease in the concentration of the salt which is neutralized by more salt going into solution. Removal of water increases the concentration and the equilibrium is restored by elimination of the excess of salt. Since it is easier to measure concentrations than vapor pressures it is more familiar to every one that for each temperature there is a single well-defined solubility than that the same is also true for the pressures. In one case it is easy to show the applicability of the Phase Rule to the rela-

tion between pressure and temperature. There should be but one temperature at which the vapor pressure of a monovariant system can be equal to the atmospheric pressure, and it is found experimentally that the boiling point of a saturated solution is constant so long as the three phases are present and the barometric pressure remains unaltered. The concentration of the solution changes with the temperature and the direction of this change can be foretold from the Theorem of Le Chatelier. If the solid dissolves with absorption of heat, it will dissolve in greater quantity if the temperature of the system rises, as this change involves addition of heat.

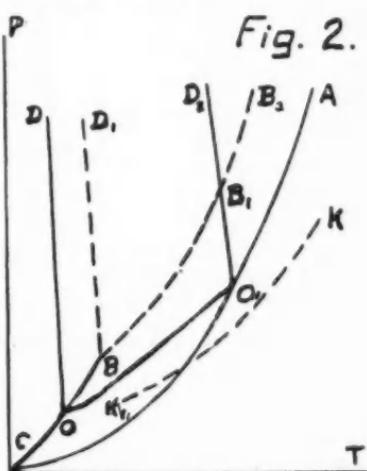
Since most salts dissolve in water with absorption of heat, the increasing solubility with rising temperature is just what one would have expected. There are substances known, such as calcium hydrate, sodium, cerium and thorium sulfates, and calcium isobutyrate which evolve heat on going into solution, and, in all these cases, there is decreasing solubility with increasing temperature. As it is not necessary that the heat of solution should have the same sign at all temperatures, it is possible for the solubility of a salt to increase with rising temperature and then decrease as the temperature rises still higher or *vice-versa*. Examples of the first type are calcium sulfate which reaches a maximum solubility between thirty and forty degrees, and calcium isobutyrate which has a maximum solubility in the neighborhood of 80°. . . .

## Hydrated Salts

If we drop the condition that the solvent and solute shall not crystallize together, a number of new solid phases become possible introducing distinct changes in the conditions of equilibrium. It will be best to confine the discussion for the present to the cases in which the two components crystallize in definite and multiple proportions, in other words with formation of compounds and not of solid solutions. When the solvent is

water, the compound formed is called a hydrate or a hydrated salt and the water is termed water of crystallization. It is possible also to have benzene, alcohol, ammonia, hydrochloric acid and many other volatile substances crystallizing with a practically non-volatile body in definite, discontinuous amounts. . . . As an example of the changes in equilibrium introduced by the possibility of the solvent and solute crystallizing together we will consider the case of sodium sulfate which crystallizes from aqueous solutions in the form of  $\text{Na}_2\text{SO}_4$ , of  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  and of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , depending on the conditions of the experiment. The pressure-temperature diagram for sodium sulfate and water is shown in Fig 2. It is not drawn to scale.

Fig. 2.



► SALTS WHICH CRYSTALLIZE with definite quantities of water of crystallization form phases which can be dealt with by means of the same type of pressure-temperature curves. Here sodium sulfate, which can separate from its solutions in three forms, anhydrous and with seven or ten molecules of water, is diagrammed to show the four possible monovariant systems which it forms.

$\text{OO}_1$ ,  $\text{OB}_1$ ,  $\text{OC}$  and  $\text{OD}$  are the curves representing the equilibria for hydrate, solution and vapor; ice, solution and vapor; hydrate, ice and vapor; hydrate, ice and solution.  $\text{O}$  is the cryohydric point just as in Fig. 1 and the remarks in regard to the equilibrium between potassium chloride and water apply to these four curves also, there being no change introduced by the presence of a hydrated salt instead of an anhydrous one. If, however, we add heat to the system hydrate, solution and vapor, kept at constant volume, there will be a rise of temperature and pressure, the system passing along the curve  $\text{OO}_1$ . At  $\text{O}_1$  a new solid phase appears in the form of the anhydrous salt and there is present a new non-variant system composed of hydrate,

anhydrous salt, solution and vapor. The point  $O_1$  is therefore an inversion point and must be situated at the intersection of four boundary curves. This is the case and the curves  $OO_1$ ,  $AO_1$ ,  $CO_1$ ,  $D_2O_1$ , represent the possible temperatures and pressures for the four monovariant systems, hydrate, solution and vapor; anhydrous salt, solution and vapor; hydrate, anhydrous salt and vapor; hydrate, anhydrous salt and solution.

The temperature at which the non-variant system can exist is  $32.6^\circ$  and the pressure 30.8 millimeters of mercury. Any continued supply or withdrawal of heat or work results finally in the disappearance of one of the four phases without change of temperature or pressure. The curve  $AO_1$ , if prolonged, will be found to lie below the curve  $OO_1$ . Since it represents a labile equilibrium at all temperatures below  $32.6^\circ$ , we see that here the less stable system has a lower vapor pressure than the more stable one. Although this is contrary to our previous experiences, it is a perfectly general result. . . .

From the existence of these two solubility curves at a given temperature, say  $30^\circ$ , it is clear that it is not sufficient to speak of a saturated solution without defining the solid phase with respect to which it is saturated. As has been said, the solution saturated at  $30^\circ$  with respect to anhydrous sodium sulfate contains more of the solute than the solution saturated with respect to  $Na_2SO_4 \cdot 10H_2O$  and is therefore in a state of labile equilibrium, stable only so long as no solid hydrated salt is present. There is yet another saturated solution which

can exist at this temperature, the solid phase being  $Na_2SO_4 \cdot 7H_2O$ . This system is unstable both with respect to the anhydrous salt and to the decahydrate, being more soluble than either. The vapor pressure of the solution is therefore less than that of either of the other solutions and is represented by the dotted line  $KK_1$ . This monovariant system differs from the other two in that at no temperature does it represent a state of stable equilibrium. In this it is analogous to the yellow phosphorus which is labile both as solid and as liquid. The crystals of  $Na_2SO_4 \cdot 7H_2O$  can be obtained by addition of alcohol to a mixture of sodium sulfate and water.

From the diagram we can predict the behavior of hydrates of this type when heated. When the temperature of the point  $O_1$  is reached the hydrate will seem to melt with precipitation of salt, forming the nonvariant system, hydrate, anhydrous salt, solution and vapor, a further addition of heat causing the disappearance of the hydrate. The temperature at which this change takes place in such salts as sodium sulfate and sodium carbonate is not the melting point of the hydrate but the inversion point. Later we shall study hydrates which have true melting points. Hydrate and vapor, being a divariant system, can exist at more than one pressure for a given temperature, and it may be well to specify in words the conditions under which hydrates change when exposed to the air. We have already seen that an anhydrous salt is permanent when the pressure of water vapor in the atmosphere is less than the pressure of the saturated

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solution and is deliquescent when it exceeds that value. Since the field for hydrate and vapor lies between  $O_1C$  and  $O_1OC$  it follows that at all temperatures, above that of the cryohydric point  $O$ , a hydrated salt will effloresce when the partial pressure of water vapor in the atmosphere falls below the pressure of the system, hydrate, effloresced salt and vapor; will deliquesce when it exceeds the vapor pressure of the saturated solution and will be permanent at intermediate values. Whether the range of pressures over which the hydrate is permanent is an extended one or not depends on the relative positions of the curves  $O_1O$  and  $O_1C$  at the temperature of the experiment. At temperatures below that of the cryohydric point the hydrate will effloresce under the same conditions as before; but if the pressure of aqueous vapor in the atmosphere exceeds the value of  $OC$  for that temperature, there

will be a precipitation of ice, the hydrate remaining unchanged.

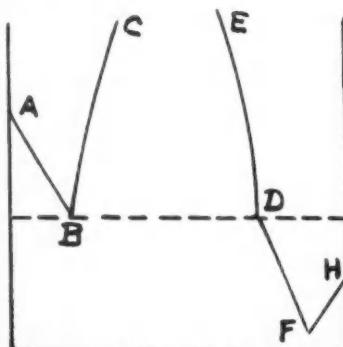
The general results which have just been obtained are not confined to reactions between salts and water. The same phenomena will recur in all cases in which the solute and solvent form a solid compound, provided that it is not possible to have two co-existing liquid phases, a case which will be treated by itself. It is to be remembered that if each component has a perceptible vapor pressure this will have an effect on the extent of the fields in which the different divariant systems can exist. The phenomenon of a constant vapor pressure at each temperature for the system, hydrate, effloresced salt and vapor, will occur in all cases in which a solid compound dissociates into a solid and a vapor. This has been shown to hold for the compounds formed by the action of ammonia on the silver haloids, on ammonium bromide and on metallic sodium. . . .

## Two Liquid Phases

There are many substances which are not miscible in all proportions in the liquid state, and, with two components of this class, it is possible to have two liquid phases, one containing an excess of one of the substances, the other of the other. The component which is in excess is in all cases the solvent, the other the solute and it is customary to speak of one of the liquid phases as a solution of A in B and of the other as a solution of B in A. As an example of this class we will take naphthalene and water. Fig. 3 gives an approximate representation of the

change of concentration with the temperature. The diagram lays no claim to accuracy because the solubilities have not been determined. AB is the fusion curve for naphthalene in the presence of water. Naphthalene is the solvent and water is the solute, the latter lowering the freezing point of the former. When the concentration represented by B is reached, further addition of water brings about no further depression of the freezing point. Instead, there appears a second liquid layer having the concentration represented by the point D, forming the

Fig. 3.



► Two LIQUIDS which form immiscible layers, each consisting of a solution of a very small amount of one of the liquids dissolved in a large amount of the other, produce two curves showing the behavior of each of the liquid phases in equilibrium with its vapor as temperatures and pressures affect freezing and boiling points.

nonvariant system, solid naphthalene, solution of water in naphthalene, solution of naphthalene in water, and vapor. The temperature at which this is possible is about  $74^{\circ}$ . This system can exist only at one temperature and one pressure. Any change in the conditions of equilibrium brings about the disappearance of one of the phases before either temperature or pressure can change. If the solid phase be made to disappear we have the monovariant system, two liquid phases and vapor. For a given temperature the pressure of the system and the concentrations in the two liquid phases are entirely

determined and addition of either water or naphthalene produces a change in the relative masses of the phases, not in their compositions. These latter are represented by the curves BC and DE. It would be possible to take either curve as representing the monovariant system and disregard the other but it conveys more information to have both in the diagram, and the points at which an isothermal line cuts the two curves show the concentrations of the two solutions in equilibrium.

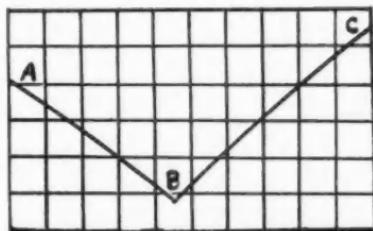
Since the two solutions and the vapor constitute a monovariant system they must have a constant boiling point so long as the external pressure remains constant. This is found to be true experimentally, the boiling mixture distilling at constant temperature—in this case at about  $95^{\circ}$ —so long as the two liquid phases are present.

It is to be noticed that there are two sets of solutions represented by BA and BC in both of which naphthalene is solvent. The first is a fusion curve, the second a solubility curve. The distinction between them is that in the latter case the solution is saturated in respect to the solute, in the former in respect to the solvent.

If a mixture of naphthalene and water forming two liquid phases and vapor be allowed to cool at constant volume, the temperature will fall until the solid naphthalene begins to appear at  $74^{\circ}$ . The temperature will remain constant until the whole of the liquid phase, solution of water in naphthalene, has disappeared leaving the monovariant system, solid naphthalene, solution of water in naphthalene.

lene, and vapor. The temperature falls again, the system passing along the line DF until at F the cryohydric point is reached and ice separates, forming the nonvariant system, naphthalene, ice, solution of naphthalene

Fig. 4.



► TWO SUBSTANCES blend in all proportions to form a series of solid solutions whose melting points become lower and lower as the mixtures approach some intermediate composition whose melting point is the minimum for the system. This is called a eutectic point. If the substances are metals, the blend with the minimum melting point is called a eutectic alloy. . . .

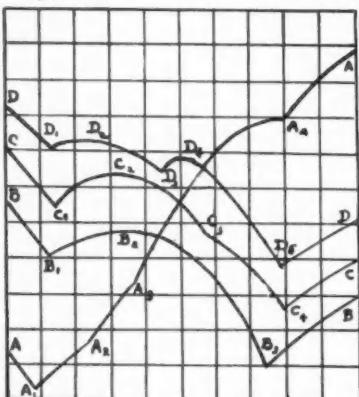
### Eutectic Alloys

Since metals are not soluble in ordinary solvents, they are often looked upon as forming a class by themselves, and it is tacitly assumed in many cases that the behavior of alloys is not described by the theorems applicable to ordinary chemical phenomena. This is a mistake. All the conclusions in regard to binary systems which have been reached in the previous discussion might have been illustrated by taking suitable pairs of metals. Addition of one metal to another lowers

in water and vapor. The temperature now remains constant until the whole of the solution has disappeared. DF is a continuation of ED, the break in the curve at D being caused by the change in the heat of solution when the solute separates in the solid state. In the solutions represented by ED and DF, water is solvent and naphthalene is solute. The curve FH is the fusion curve for ice. The complete concentration-temperature diagram for two substances, which do not form any compounds and which do form two liquid phases at some temperature, consists of two fusion curves and two solubility curves. In the fields ABC and EFH there exist the divariant systems, solution and vapor. In the first, naphthalene is solvent; in the second, water. These systems may have either higher or lower vapor pressures than the pure solvents. The relation of these vapor pressures to those of the monovariant systems, two liquid phases and vapor is made clear by following the change of pressure with the concentration at constant temperature. . . .

the freezing point of the second if the pure solvent separates. If two metals form neither compounds nor solid solutions and are consolute in the liquid form, the nonvariant system, two solids, solution and vapor, will be possible at one temperature and pressure only, and that temperature will be lower than the freezing point of either of the pure components. If a mixture of two such metals be heated until completely liquefied and the molten mass allowed to cool slowly, a

Fig. 5.



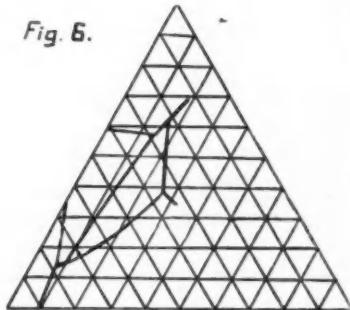
► FOUR DIFFERENT TYPES of curves are shown here for the freezing points of systems with two components which can combine to form compounds but not solid solutions. In diagrams of this type, the margin at the left-hand side represents one pure component, that at the right the other. Systems combining the two components are plotted in the area between, the distances from the two sides being proportional to the amounts of each present.

sudden change in the rate of cooling will be noted at a temperature which varies with the original composition of the solution; at a lower temperature the temperature will remain constant until all the metal has solidified. The change of rate occurs when one of the metals crystallizes from the

Mexico has approximately 50,000,000 acres of timberland; its forest cover in general is light, but according to estimates contains 75,000,000,000 board feet.

solution and is therefore a function of the concentration. The constant temperature comes at the eutectic temperature. Examples of this are lead and silver, lead and bismuth, tin and bismuth, zinc and tin. The fact that one of the metals separates in the pure state until a certain concentration is reached, is made use of technically in the Pattinson process to enrich silver ore. An ore rich in lead and poor in silver is melted and allowed to cool to the eutectic temperature when the liquid is poured off. During the cooling, pure lead crystallizes and the concentration of silver increases to the value corresponding to the eutectic alloy.

Fig. 6.



► THREE-COMPONENT systems are plotted on an equilateral triangle, the length of each side taken equal to 100 parts. The curves shown on such a diagram trace the composition of systems made up of varying proportions of the components which are stable at a given temperature and pressure.

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## Bitter Salts and Amino Acids Removed by Granulated Resins

# Sugar Syrups by Ion Exchange

Reprinted from "For Instance," American Cyanamid Company

► BEVERAGE BOTTLERS and confectioners are reporting success in using sugar syrups derived from the converted starches of corn, wheat, rye or potatoes, which have been purified by passing them through beds of ion exchange resins. Untreated syrups from these sources each have their own characteristic tastes, most of which are damaging to other flavors and difficult to mask. The offensive tastes are due mostly to the presence of proteins, organic acids and bitter potassium salts. Calcium, magnesium, and a number of other inorganic elements are also contributing factors. These culprits were identified long ago but there has been no practical and economical way of removing them. Such syrups have been interesting but very limited in the number of their uses. Now however, in the trial installations, they are giving up their undesirable native contents to successive ion-exchange resin beds and emerging without objectionable taste or odor. Maltose syrup, for instance, with its dark color and high malt flavor, unsuitable for ice cream, is, by mere passage through the resins, being routinely turned into an almost water-white product of higher sweetening value.

Except for evaporation of the syrups to any desired final concentration, no heat is required and only a minimum of attendance; the syrup merely moves continuously through successive beds at suitable speed, giving up bitter salts

and acids to the ion exchange resins. The resins look like colored sands and the grains are too hard to suffer from attrition by the moving syrup. The effluent syrups can be made clear and colorless. They are sufficiently free of inorganic salts and amino acids which promote the growth of yeasts and molds, hence the stability of the syrups is improved. Crystallization is easily inhibited, if necessary, by controlling the concentration.

Thus the sugar syrup user can obtain all the various types of syrup free of any taste but simple sweetness, as a dependable base for his flavoring and further processing.

Success of this method follows logically from its recently demonstrated effectiveness in the refining of raw cane and beet sugar juices where it has drastically simplified the processes and increased the yields of white sugars.

Ion exchange has come into wide use to demineralize tap water, producing a water that is chemically comparable to distilled water, but much cheaper. When brackish water, for example, is filtered through granular beds of the resins, the first bed splits the salt, (sodium chloride, for instance,) by taking up the sodium in exchange for hydrogen, and the next bed, a different resin, takes up the hydrogen chloride. Likewise with potassium and calcium salts and the other familiar acid-base (i.e. salt) com-

binations found in ground water everywhere. The resin beds are provided in great relative mass compared with the traces of salts they split and capture, but saturation of the resins develops at intervals, and the resin beds are then easily and cheaply regenerated to their original effectiveness by drenching the alternate resins with acid and alkali respectively. Thus

tap water in laboratories flows through a set of four little filter columns and emerges demineralized, factories improve their boiler water and process water, or a mountain village gets potable water, by putting mine water through an installation of larger resin beds. Ion exchange resins went into many such commercial installations last year.

## *Polluted Waters Harm Factories*

► STREAM pollution from wastes from chemical and other industries is a costly nuisance to other manufacturing plants forced to use the polluted water in their manufacturing processes and in their boilers and other equipment. It is a danger to public health, also, and an injury to the recreational value of a stream.

A summary of these costs to industry was reported to the American Institute of Chemical Engineers meeting at Atlantic City by Charles F. Hauck of Pittsburgh, and other chemists presented aspects of waste disposal problems.

Plants compelled to use grossly contaminated water must either pay more for suitable water or bear the penalty of using objectionable water. Using impure water results in higher maintenance costs on equipment and, less frequently, lowers the quality of the products or the efficiency of operation. The expense absorbed annually by industry from the use of contaminated water amounts to millions of dollars.

The answer to the pollution nuisance is to require all plants discharging wastes into streams to treat the

water chemically before discharge. By so doing not only is contamination prevented but valuable chemicals may be recovered.

Elimination of major pollution would require an initial capital outlay of \$800,000,000, Mr. Hauck estimated, and an annual estimated outlay of \$225,000,000 for operation of the equipment for treatment and disposal.

Even the dairy industry is guilty of stream pollution. The disposal of five types of liquid dairy wastes was discussed by H. A. Trebler and H. G. Harding of the National Dairy Products Corp., Baltimore. They described equipment used in one dairy in recovering wastes from domestic waste, cooling waters, spoiled or excess products, drips, leaks, rinse and wash waters.

T. J. Powers, of the Dow Chemical Co., reported that 75,000,000 gallons of water are treated each day by his company. Two thirds are satisfactorily handled by sedimentation, aeration with secondary settling and active sludge return. Phenolic wastes of 25,000,000 gallons a day are treated through strong waste storage pond, primary sedimentation, filters and a sludge plant.

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## English Glass Technologist Tells New Methods in an Ancient Art

# Color in Glass

Reprinted from ENDEAVOUR, London

L. M. ANGUS-BUTTERWORTH

*The making and working of coloured glasses are among the world's most ancient crafts. Although the empirical methods of the early workers produced results of great beauty, the study of the chemical processes involved has proved a fruitful field of research. The present extensive use of*

*coloured glasses in scientific apparatus, signalling lamps, photographic filters, and other equipment demands a standardized product which is obtainable only as a result of knowledge of the chemical reactions involved and careful control of manufacturing processes.*

► THE HISTORY of coloured glasses is longer than that of the transparent white variety. For many centuries before clear glass appeared a large number of different coloured forms had been in common use.

Some of the glazed tiles covering the walls of early Egyptian chambers were magnificent examples of colouring, and polychromes as well as single colours were achieved. Pieces have been found of a vase, bearing the name of a king living in 5000 B. C., which was glazed in green inlaid with purple. Some of the most important colouring oxides employed in glass-making today, including those of copper, manganese, and cobalt, were known to the Egyptians. Transparent glass did not appear in Egypt before about 660 B.C., when bottles and a few other objects were made of it.

From these early beginnings in Egypt the art of coloured glassmaking gradually spread. One of the first uses of coloured glass in England was in cathedral windows.

A common belief is that we do not

know today how to reproduce the brilliant colours of the early cathedral windows. This was partly true up to about a hundred years ago, but today the glass technologist certainly knows far more about colours in glass than was ever known before.

A further point in connection with old cathedral glass is that when originally placed in position it was often very crude in colour and dark in shade. It has taken hundreds of years to become mellowed. Atmospheric attack on the outside of church windows has been the chief agent in creating the beautiful effects we know today. Throughout the centuries there has been steady abrasive action through the rain being driven against the glass by the wind, and chemical dissolving action through the slight acid content of much of our rain water, especially in towns. The combination of these two forces has gradually changed thick and comparatively dark glass to glass which in some cases is as thin as tissue paper and which now has light and vivid colours.

Even the impurities in the metals, which the early glassmakers could not control, gave variety to their products. It was of little consequence if the glass they supplied for church windows never had quite the same colour twice. Exciting surprises were possible—not as in the dull modern world, in which glass making materials and processes are so carefully and completely controlled that results are (or should be) well ascertained in advance.

It is convenient to consider the agents for the production of each of the common colours in glass in turn.

### Black

Cobalt and nickel oxides are used together to give opaque black glasses. Nickel glasses are noted by Professor Woldemar Weyl as absorbing nearly the entire visible spectrum with the exception of the extreme red.

A small antique glass bowl of an almost jet-black colour shown to the author on one occasion by the late Sir William Boyd Dawkins had certainly a high concentration of manganese as the principal colouring agent, possibly with the addition of a little cobalt.

### Blue

Cobalt and copper serve as the usual agents for colouring glasses blue. Of the two, cobalt is the more commonly used. It transmits a deep red band in addition to blue. Accordingly, if a cobalt blue is combined with a copper bluish green, the latter absorbs the red and an excellent blue glass is obtained. If, however, the colour required is to be midway between blue and green, as in signal lenses, copper is used in association with a small amount of iron.

Weyl observes that from the viewpoint of glass technology we need only consider cobalt compounds which are derived from the bivalent cobalt ion, as tervalent cobalt is not stable in the temperature range required for glass melting. It has been found that potash glasses give a purer blue than the corresponding sodium glasses, and that borosilicates yield a reddish hue.

An interesting modern use of cobalt is in connection with glassware for lighting. If small amounts of cobalt, manganese, and copper oxides are used together in the batch, what is now known as the daylight effect is obtained. What happens is that these oxides eliminate part of the light from the artificial light sources, and the filtered remainder more closely resembles natural sunlight.

Sir Herbert Jackson suggested that the production and properties of glasses containing copper are representative of those in which the colouring is diffused in very minute particles throughout the glass, and which can be compared with colloidal solutions. In contrast to this, cobalt glasses are examples of those in which the colouring agents are in a state resembling solution, which might be compared to aqueous solutions of coloured salts.

Gmelin noted in 1779 that glasses containing iron became blue when founded under strongly reducing conditions, but no explanation was then possible. The colour was later attributed to a modification of ferric oxide which is stable only in the presence of ferrous oxide. This involves the existence of the two states of valency in

the glass, or the simultaneous presence of  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ . The addition of limestone to the melting glass may cause the colour to change to blue, as it may contain some material which acts as a reducing agent.

### Green

For the production of green glasses iron, copper, and chromium are employed. Other possible agents, such as stannic oxide, are very rarely used.

The presence of 0.23 per cent.  $\text{Fe}_2\text{O}_3$  gives an almost colourless glass which is greenish-blue in thick layers; 0.48 per cent. a light sea-green; 0.73 per cent. a bright sea-green; 1.23 per cent. a bright yellowish-green; 5.56 per cent a deep yellowish-green, but still transparent; 8.23 per cent. a dark olive green, still transparent even in thick layers; 11.12 per cent. a dark olive green, but opaque in thick layers. The percentages stated were obtained by the analysis of test glasses, and therefore represent the amount of iron present in the finished glass.

As might be expected, the colours given by copper depend upon the conditions under which the glass is melted. A blue or green glass is obtained from copper compounds under oxidizing conditions and a ruby colour under reducing conditions. For green glasses the black or cupric oxide is used.

Chromium was discovered in 1795 in the Russian mineral crocoite, which is a lead chromate that has been used for colouring glass since the early part of the last century. The name is derived from the Greek word *chroma* (colour) and indicates that chromium compounds have vivid hues.

### Grey

To produce grey or 'smoked' glass the colouring agents used are combinations of (a) cobalt, nickel, and uranium oxides, or (b) manganese, iron, and copper oxides. The glass may be of either the soda-lime or lead-potash type.

### Opal

Opal glasses fall into two main classes. First, that in which the opacifying agent dissolves, leaving the glass transparent while molten but causing it to become opaque upon cooling. Second, that in which the opacifier never wholly dissolves but remains very evenly and finely distributed throughout the molten metal. In the one type, the glass is quite transparent when gathered from the crucible and gradually becomes opal as it cools. In the other, the metal is already opal upon gathering but becomes more so as the temperature falls.

In most opal glasses the opacity is dependent upon the separation of either finely divided silica, or some metallic oxide, or both, from the mass of glass. The separation is assisted by the presence of fluorides and phosphates. A certain degree of opalescence may result from the separation of the fluoride (say as aluminum fluoride) or the phosphates themselves from the glass, but as a rule the batch is such that they remain combined as fluo-silicates and phospho-silicates throwing the silica out of solution. The source of the opal colour in glass, therefore, may be either excess of silica, excess of a metallic oxide, e.g. of aluminum, tin, or antimony, or the presence of fluorides or phosphates.

Duval d'Adrian has sought to show that, by using the complex fluorides of silicon, boron, tin, zirconium, and titanium with the fluorides of the alkaline earths and heavy metals, and adding various mixtures of these to an ordinary glass batch, more satisfactory results are obtained than with simple fluorides.

Opal glass is being increasingly used for a wide variety of purposes. It is now commonly found in the form of illuminating globes and bowls, sheet glass, towel rails, imitation candle tubes for electric lighting, containers for pomades and other druggists' sundries, and linings for electroplated articles.

### Orange

According to Sir Herbert Jackson, the famous Chinese *sang-de-bœuf*, or oxblood, glazes were due to dispersed finely divided copper in amounts of the order of 0.5 per cent., the reducing conditions under which they were made preventing any tinge of green through the presence of cupric oxide.

### Purple

The compounds of manganese are among the oldest colouring agents used in glass. Dralle and others have stated that the purple colour is produced by the tervalent manganese oxide,  $Mn_2O_3$ , in equilibrium with  $MnO$ . To secure a deep colour with manganese the founding has to be under oxidizing conditions, as reducing agents destroy the purple tint.

Two pieces of transparent glass of an intense purple colour were sent to the late Sir William Crookes from South America. They had been found on rubbish heaps at a high altitude and had been exposed to the action

of the sun over a long period. The probable cause of the colour was manganese, which would be affected by the solar rays of short wavelength, present at an altitude of 4,000 metres but absent at sea-level owing to atmospheric absorption. The colour had penetrated the whole mass, but disappeared when the glass was reheated to softening-point. By exposure to radium rays the colour could quickly be reproduced.

### Red and Ruby

Copper oxide in the cuprous form, melted under reducing conditions, gives an excellent ruby. If a copper ruby is reheated slowly for some time the particles of copper aggregate and become visible to the naked eye, giving what is known as an aventurine glass. This type of glass was first made at Murano, the name 'aventurine' being from the Italian *avventurino* (chance), indicating its accidental discovery. It has been described as a semi-opaque glass filled with golden yellow spangles.

On the rare occasions when a gold ruby glass is made today it is generally prepared from a soft lead batch containing an excess of antimony and arsenic. The gold is added in the form of a solution of gold chloride, in the proportion of 1 oz. of metal to 200 lb. of batch.

Selenium was first isolated in 1817 by Berzelius, who used the mud of sulphuric acid plants as his raw material.

Although selenium is now being used more and more as a source of red colour in glass the colour is difficult to retain, because if great care is not taken the selenium has a strong tendency to volatilize.

## Violet

Colours ranging from violet to purple can be obtained by adding less than 1 per cent. of titanium dioxide ( $TiO_2$ ) to the batch mixtures of certain borosilicate or phosphate glasses.

## Yellow and Amber

It is believed at present that no single element can be used to isolate spectral yellow in glass. Glasses of varying shades of yellow are, however produced by means of cadmium, silver, sulphur, and uranium.

Carbon is very commonly used in the manufacture of yellow glasses, being introduced in the form of coke, graphite, or anthracite. It is the sulphate-containing impurities in the carbon which are the true source of the colour. This was demonstrated among others by Splitzerber, who in 1839 melted two carbon-containing batches, the first of which had 1.75 per cent. of sodium sulphate but the other

none, and only the former developed a yellow colour. Again, in 1865, Pelouze obtained similar results.

In the making of amber glasses it is usual to employ a mixture of sulphur and charcoal as the colouring material. The batch must of necessity be melted in a reducing atmosphere. Experiments by Fenaroli and others led to the conclusion that the elements of the group giving yellow colours are effective in colouring glasses only when they are present as polysulphides, polyselenides, or polytellurides.

It was in 1789 that Klaproth isolated a new element, uranium, from the mineral pitchblende. He obtained sodium uranate as a bright yellow precipitate, which soon came to be used as a colouring agent for glass and glazes. When available, uranium can be used with antimony to give a stable yellow in glasses containing lead.

## *Lignin Successfully Used With Fertilizers*

► **LIGNIN**, a by-product of pulp and paper mills that has long been regarded as "the largest waste in industry," is now found useful with fertilizers to add humus and organic matter to depleted soils.

This new use of lignin, reported by Robert S. Aries, research associate at Yale University, is important because of the tonnage involved. Lignin is an organic substance which, with cellulose, forms the chief part of woody tissue.

In addition to 2,000,000 tons of lignin now discharged annually by mills into streams and rivers, sawmills and other woodworking plants throughout the country "can readily make avail-

able another 10,000,000 tons of wood waste which can readily be incorporated into fertilizers."

Lignin may assume an important part in this nation's soil building and conservation program. Lignin at present pollutes the nation's rivers; as fertilizer, it will definitely aid in providing higher land values and richer soils."

The part played in soil improvement by using lignin with fertilizers is largely to supply organic matter. If lignin is used on presently fertilized soils which need humus and organic matter, it is estimated that the efficiency of these soils would be raised about 20 per cent.

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